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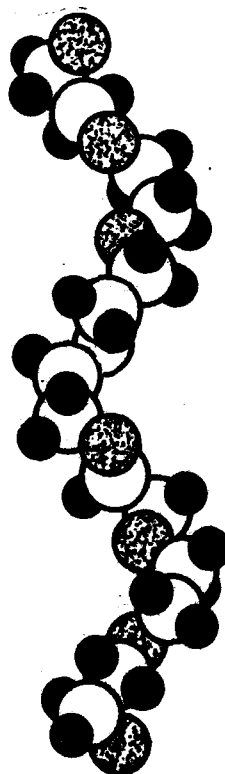
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**FIRST
INTERNATIONAL SYMPOSIUM
ON
POLYMER ELECTROLYTES**

AD-A223 013

US ARMY RESEARCH, DEVELOPMENT & STANDARDIZATION GROUP



**St. Andrews
Scotland**

**June
1987**

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INTERNATIONAL SYMPOSIUM ON POLYMER ELECTROLYTES

ISPE 1

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St. Andrews

June 1987.

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INSIGHTS INTO ION-MATRIX, AND ION-ION,
COUPLINGS IN POLYMER SALT ELECTROLYTES
FROM RELAXATION SPECTROSCOPY

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This talk is motivated by the need to contrast mechanisms of relaxation in different potential solid state electrolyte systems in a simple self-consistent manner. To this end we will examine the available transport data on polymer-salt systems in terms of the characteristic relaxation times for applied electrical fields (which determine the d.c. conductivity of the solution) and the relaxation times for mechanical stress (which measure the rate at which the matrix itself deforms in response to applied mechanical stresses). These times may be obtained by means of various relaxation spectroscopy techniques or, as average values, from d.c transport properties in some cases. In the case of fast ion conducting glasses the inverse ratio of these two times has been called the *decoupling index*, and its value has been used to distinguish the potential of one sort of glassy system from that of another. Systems favorable for practical applications are those which have decoupling indexes of the order of 10^{13} at around the temperature of application.

In polymer-salt systems the determination of the appropriate mechanical relaxation time requires some thought since the macroscopic viscosity in high molecular weight systems may not reflect at all the relaxation time for mechanical stress felt at the molecular level. Different techniques for obtaining the microscopic mechanical relaxation time are discussed and the resulting values are compared with the conductivity relaxation times for different polymer-salt systems. In the most favorable cases we find decoupling indexes of the order of unity, reflecting the well known fact that the migration mechanism in these systems is totally different from that in ionic glasses. In cases of weak electrolytes, the decoupling index can be substantially less than unity, reflecting the coupling of ions to themselves (ion-pairing) as well as to the matrix. Finally we examine some novel plastic crystal-plus-salt systems in which the *decoupling index* is of the order of unity and in which the conductivity relaxation time at room temperature is shorter than to that in all other coupled systems. The relative merits of polymeric salt versus plastic-crystal-salt systems, which in fact have many features in common, will be examined.

DIFFUSION OF IONS ON POLYMER ELECTROLYTES

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The discovery [1] of a relatively high ionic conductivity in complexes formed between polyethylene oxide and alkali metal salts and the proposed applications [2] of these materials as battery electrolytes has invoked considerable interest in polymer electrolytes. The nature of the ionic transport processes in these systems is of fundamental importance and this is a complex problem to resolve. Experimental investigations of the ionic transport have predominantly used electrical conductivity measurements, however, in isolation they reveal little on the microscopic processes involved in ion migration or even the nature of the charge carrier. In crystalline ionic conductors considerable detail is known about the ion migration processes [3,4] and prime sources of this information have been methods which involve direct studies of the diffusion of ions. Recently, these types of study have been reported for polyether electrolytes [5]. Although this work to date is limited to relatively few systems it has provided vital data on the mobilities of ions and potential transport mechanisms. The objective of this contribution is to review these investigations.

The first section of this review will concentrate on the experimental techniques available for the measurement of diffusion coefficients in polymer electrolytes; these are primarily radiotracer and nuclear magnetic resonance methods. The coverage will include an outline of the basic principles of the techniques, the equipment and sample requirements, and the analysis of the raw data. Special emphasis will be given to the advantages and limitations of each technique.

In the second section consideration will be given to the use of diffusion data as a probe of ion migration mechanisms. This will include a description of the Haven ratio approach [5,6], which combines diffusion and conductivity measurements. In essence, the two measurements are compared via the Nernst-Einstein equation and deviations provide information on the extent of correlation between diffusive steps of the ions [7]. The degree of correlation itself depends on the migration mechanism. Other approaches which have proved fruitful as mechanistic probes of ion transport in crystalline solids are the

1.2

effect of pressure on diffusion [8] and the effect of isotopic mass on diffusion [9]. The possible application of these methods to polymer electrolytes will be included in this section.

Finally, the available diffusion data will be reviewed and their implications in terms of the diffusion mechanisms will be discussed.

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COMB SHAPED POLYMER ELECTROLYTES

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INTRODUCTION

Work on polymer/salt mixtures has increased dramatically during the past decade due to the interest in these systems as fast ion conducting systems. One of the most successful of the host polymer matrices, capable of dissolving inorganic salts to produce homogeneous mixtures, is poly(ethylene oxide) PEO. It has been studied widely in the pure homopolymeric form but it tends to form semicrystalline mixtures at temperatures below 350K. Consequently many workers have concentrated their attention on a variety of alternative structures containing short PEO chain segments, thereby avoiding the propensity for PEO to crystallize. These structures include block and graft copolymer networks and comb-shaped polymers with short pendant PEO chains attached to backbones based on poly(methacrylic acid),^(1,2) poly(itaconic acid),^(3,4) polyphosphazene⁽⁵⁾ and poly[oxy(methyl silene)].⁽⁶⁾

Our interest has centred on the polyitaconate derivatives but recently this has been extended to an examination of comb-shaped structures based on poly(ethylene oxide) macromers and polyphosphazenes with pendant crown ethers.

POLYITACONATES

Comb-shaped esters of polyitaconates with 1,2,3, and 7 methoxy terminated ethylene oxide [EO] units attached to each monomer unit were synthesised. The variation of the glass transition temperature T_g with added salt is shown in Figure 1(a) and (b) for NaClO_4 and LiClO_4 respectively. The lowest range of T_g values is observed for the structure with seven EO units. The structures with one EO unit show little variation of T_g with salt and the values are generally higher than those for the longer side chains. The conductivities in these systems are highest for the lowest T_g mixtures as can be seen from Figure 2, where $\log(\text{conductivity}) (\sigma)$ is greatest for the structure with seven EO units and decreases to a very low level for the structure with only one EO unit. These data

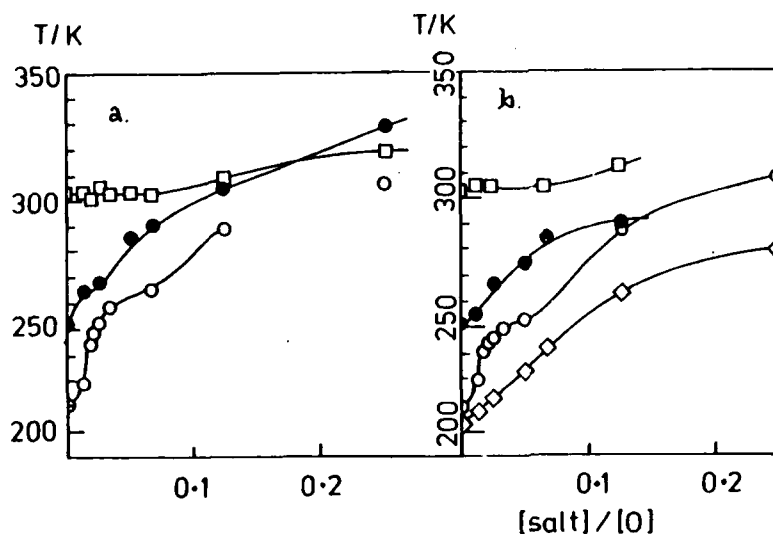


Figure 1(a): Variation of T_g with added NaClO_4 for poly-itaconates with one (\square); two (\bullet); and three (\circ) ethylene oxide units in each side chain.

Figure 1(b): Variation of T_g with added LiClO_4 for poly-itaconates with one (\square); two (\bullet); three (\circ) and seven (\diamond) ethylene oxide units in each side chain.

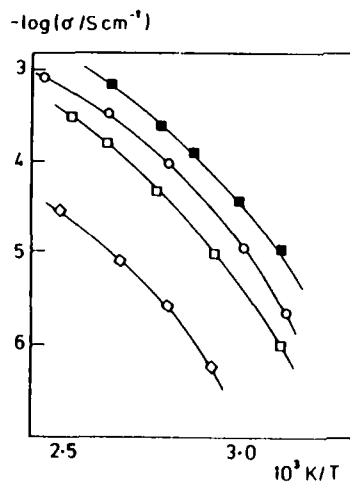


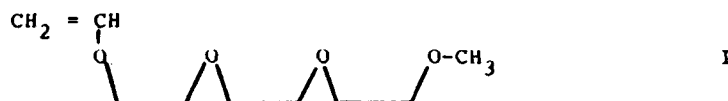
Figure 2: A logarithmic plot of conductivity (σ) as a function of reciprocal temperature for poly itaconates with one (\diamond); two (\square), three (\circ) and seven (\blacksquare) ethylene oxide units in the side chain.

are for mixtures with NaClO_4 at a ratio $[\text{Na}^+]/[\text{EO unit}]$ of 0.125.

For the polyitaconates, the optimum side chain length would appear to be about seven ethylene oxide units as longer side chains will be prone to crystallization.

POLYMERS FROM ETHYLENE OXIDE MACROMERS (PVEO₃)

Polymerization of structure I gave material with $M_n = 30,000$ which dissolved many inorganic salts to give amorphous homogeneous mixtures.



The T_g of these mixtures mirror the behaviour of the polyitaconates with three ethylene oxide units. An interesting comparison of conductivities in these systems is illustrated in Figures 3(a) and (b) where PVEO₃ is compared

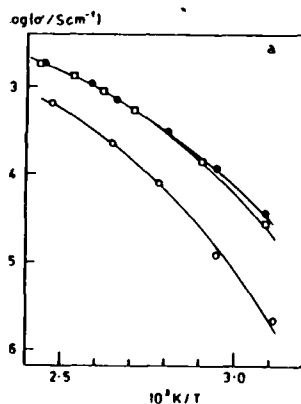


Figure 3(a): Comparison of $\log \sigma$ against $1/T$ plot for polyitaconates with three (○), and seven (□) ethylene oxide units, and PVEO₃ (●) - salt is LiClO₄ at $[\text{Li}^+]/[\text{EO unit}] = 0.125$.

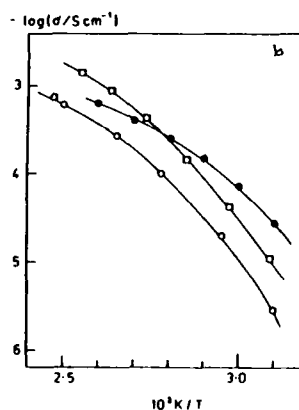


Figure 3(b): Comparison of $\log \sigma$ against $1/T$ for polyitaconates with three (○), and seven (□) ethylene oxide units, and PVEO₃ (●) - salt is NaClO₄ at $[\text{Na}^+]/[\text{EO unit}] = 0.125$.

with the polyitaconates comprising three and seven EO units in the sidechain using LiClO₄ and NaClO₄ at a $[\text{cation}]/[\text{EO unit}]$ ratio of 0.125. In both cases the conductivities observed in the PVEO₃ systems are higher than the polyitaconates with comparable side chain lengths and when LiClO₄ is the salt used the PVEO₃ mixtures have

conductivities matching those in the itaconates with seven EO units. This may be a reflection of the greater flexibility of the chain backbone in the $PVEO_3$ system.

POLYPHOSPHAZENE-CROWN ETHERS

A series of polyphosphazenes with pendant crown ethers have been prepared. A 16-crown-5 unit was attached to the polyphosphazene backbone using methylene spacer units to modify the initial Tg of the polymer. Spacers with 0, 3, and 6 methylene units were examined and the Tgs were observed to change in the order 233K, 226K and 224.5K respectively.

For the unspaced structure the increase in Tg when a salt is added is greater when $NaClO_4$ is used compared with the system containing $LiClO_4$. This is reflected in the conductivity levels which are significantly better in the $NaClO_4$ polymer system. The implication is that this crown ether is a more effective binding agent for the Na^+ than the Li^+ and so there is a larger number of charge carriers and fewer ion pairs produced in the system containing $NaClO_4$.

Conductivity levels can also be improved by lengthening the spacer and decreasing the initial Tg of the polymer as can be seen in Figure 4, where the system with six methylene units now achieves conductivity levels similar to some of the linear side chain structures.

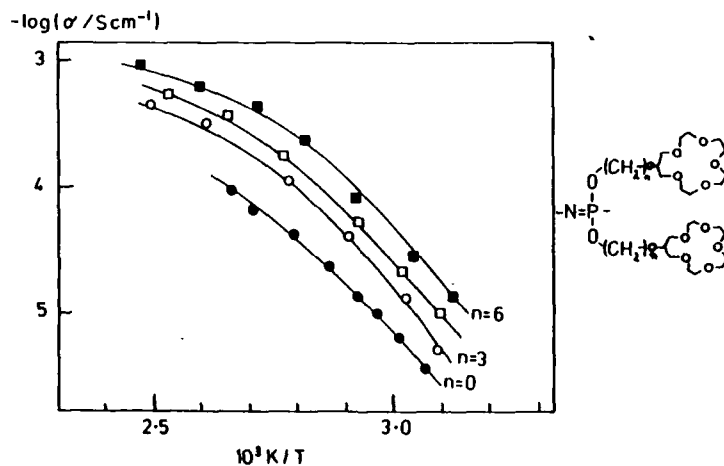


Figure 4: Effect of spacer length on the temperature dependence of conductivity 16-Crown-5 derivatives with zero (●), three (○) and six (■) methylene spacer units. Also for comparison a 15-crown-5 derivative with one methylene spacing unit (□).

It might be expected that a decrease in crown ether ring size would improve the complexing of the Li^+ ion. A structure with one methylene spacer and a 12-crown-4 ring was tested with LiClO_4 but no significant improvement in conductivity was observed. This question of ring size will be discussed more fully.

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CROSS-LINKED POLYETHERS AS MEDIA FOR IONIC CONDUCTION

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INTRODUCTION

The use of macromolecular materials as electrolytes for solid-state batteries was envisaged over a decade ago (1,2). The underlying features sought for these polymers were : good solvating power vis-à-vis the cations (which of course implies a reasonable solubility of the salt into the macromolecular system), an essentially cationic charge transport leading to conductivity as high as possible and adequate electrochemical stability.

Linear polyethers were first studied and conductivities of around 10^5 S.cm^{-1} obtained at room temperatures with various salts.

Since then many laboratories have been tackling these problems with different materials and working hypotheses. Three major drawbacks were soon encountered, viz. (i) crystallization of part of the polymer (high DP) which relegates ionic mobility to the remaining amorphous regions ; (ii) lack of dimensional stability due to creep particularly at the higher temperatures ; (iii) cationic transport numbers much lower than unity.

The approach chosen in our laboratory (3-6) called upon the basic premise that crosslinking the polyether chains would minimize crystallization and eliminate creep. As for the third drawback, ionomeric networks with anions fixed on the chains were envisaged.

This lecture will outline the results obtained with networks containing either a dissolved salt or an attached ionisable moiety. From this detailed study conclusions will be proposed concerning molecular-scale models of ion-chain interactions, the origin and mode of ionic transport and the electrochemical performances of some of these materials.

NETWORKS WITH ADDED SALT

The materials tested were essentially polyethers crosslinked by isocyanates and filled with various salts (mostly alkali-metal salts of strong acids). A wide variety of networks were prepared from different polyethers (chemical structure, linear, branched, homo- and co-polymers, DP) using different di- and tri-isocyanates and working at different synthesis concentrations.

Specific Volume

Quantitative relationships were obtained as a function of crosslink density and salt concentration, with particular emphasis on systems based on polyethylene oxide (PEO) and containing LiClO_4 . The results clearly indicated the occurrence of important interactions between the salt and the polymer chains suggesting a physicochemical association resembling (reversible, dynamic) crosslinking.

Glass-Transition Temperature

Two sets of measurements of T_g were conducted for each system, viz., the effect of crosslink density with salt-less networks and the effect of salt concentration with networks of a given crosslink density. Again the results obtained suggest physico-chemical crosslinking induced by the added salt. It seems reasonable to postulate that the cation forms a complex with the oxygen atoms of the ether functions. Thus, in the specific instance of a PEO network containing LiClO_4 , it was found that three Li^+ have the same stiffening effect as one urethane crosslink.

Swelling

Here too, both salt-less and charged networks were examined. Moreover, liquids of different polarity were used to swell the materials. Again most quantitative information was gathered with PEO-based networks and LiClO_4 as salt. It was found that with non-polar liquids the same relationships applied to salt-less and salt-containing networks if the specific effect on T_g (see above) was used as normalising factor. With more polar swelling agents the ion-chain interactions tended to fade away. These results confirmed the existence of strong polar complexes between cations (free or as multiplets) and ether groups on the polymer chains held between urethane crosslinks.

Transverse Nuclear Magnetic Relaxation

This technique, applied to the ^1H nuclei of the polymer chains, confirmed the binding role of the ionic moieties from the added salt. Indeed, an increase in salt concentration resulted in a change in response of the network indicating chain partitioning by physico-chemical crosslinking.

NMR Linewidths

This parameter was studied with ^1H , ^7Li and ^{19}F , viz. with nuclei belonging to the polymer network, the cation and the anion (e.g. CF_3SO_3^-). The changes in linewidth with temperature gave a very similar behaviour for the three nuclei and was typical of a free-volume

situation. This strongly suggests that the segmental motions within the polymer chains induce the synchronous participation of the ions situated in their vicinity.

Dynamic Mechanical Properties

All the networks tested, with and without salts, showed a typical WLF behaviour with values of C_1 and C_2 at T_g independent of all variables studied. Moreover, these values were practically the same as those calculated from the linewidth-vs-temperature experiments.

Ionic Conductivity

A large number of systems were tested in order to correlate the σ -vs- T diagrams with the variables defined above. Satisfactory conductivities, namely $> 10^{-5} \text{ S.cm}^{-1}$ at 25°C , were obtained with many systems. All trends observed were adequately explained on the basis of free-volume considerations. This implies that the ionic transport across the network under an electric field is determined by segmental motions as described by the WLF equations.

The values of C_1 and C_2 at T_g were again very close to those obtained by the two previous techniques.

Transport Numbers

It was found that the fractional cationic contribution to the overall conductivity, t^+ , was systematically well below unity, sometimes close to zero and with magnesium salts $t^+ = 0$. This clearly shows that the interactions of the cations with the ether groups are strong enough to unbalance their mobility with respect to that of the anions and even to block it completely.

IONOMERIC NETWORKS

The results summarized above show that it is possible to eliminate the problems of crystallisation and those related to creep and still obtain satisfactory levels of ionic conductivity by a judicious crosslinking of the polyether chains.

However, the drawback linked to the low cationic transport numbers persisted, as was to be expected.

We decided to prepare and test similar networks in which the ionic (or ionisable) functions would be part of their structure, with the anions covalently bound to the chains and the cations free to dissociate and migrate across the material.

These ionomers were synthesized with different structures, but mostly with phosphate and thiophosphate groups attached to polyether-urethane networks.

As expected, t^+ became unity, but the actual value of the conductivity at room temperature were lower than with salt + network systems and reached $\approx 10^{-5} \text{ S.cm}^{-1}$ at about 100°C .

These ionomeric networks showed the same free-volume behaviour as that encountered with networks filled with salts.

CONCLUSION

A model will be presented to attempt an explanation of all the major features observed in this investigation. It involves the formation of quadrupoles around an intersection of two polyether chains and the transfer of ions, through segmental motions, from one such structure to the next.

Also, an outline will be given of the electrochemical stability of some of these materials as well as of their performance as electrolytes in battery set-up.

Finally, suggestions will be put forward concerning the preparation of better ionomeric networks.

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ELECTRODE KINETICS IN CELLS BASED ON POLYMER ELECTROLYTES

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Complexes of poly(ethylene oxide), PEO, and lithium salts, have great promise as advanced, solid-state polymer electrolytes for the development of high-energy lithium batteries (1-3). This important perspective has prompted us to carry out a systematic investigation of the characteristics of the electrode materials which appear to be the most promising for the realization of this type of battery.

The kinetics of the lithium electrode in polymer electrolyte cells have been examined by a.c. impedance spectroscopy, by d.c. polarization curves and by cyclic voltammetry. The results indicate that the lithium metal electrode, even if basically reversible, suffers from passivation phenomena similar to those observed in organic liquid electrolytes (4). The characteristics of these passivation effects, as well as their influence on the cyclability of the lithium electrode in rechargeable polymer electrolyte batteries are examined and discussed.

The properties of the electrochemical processes of typical positive electrodes, such as intercalation transition metal sulphides and oxides, have been examined by voltage-composition curves and by cyclic voltammetry. Very promising behaviour is shown by the $\text{Li}_{1+x}\text{V}_3\text{O}_8$ electrode material. The basic structural elements of this bronze are octahedra and trigonal bipyramids which are arranged to form puckered layers with the Li^+ ions situated in between, occupying octahedral sites (5). The unit cell comprises six empty tetrahedral sites where excess of lithium may be accommodated with excellent structure retention. This allows good reversibility of the lithium intercalation-deintercalation process, with a maximum uptake of about 3 eq/mol.

This highly reversible behaviour has been practically confirmed by repetitive cyclic voltammetry in various polymer electrolyte media.

Furthermore, considering that polymer electrolytes with conduction by other ions than lithium may be of great importance in electronic technology, the kinetics of copper electrodes in a new family of polymer electrolytes have also been investigated. Results (6) based on a.c. impedance spectroscopy and d.c. polarization curves indicate that the copper polymer systems may eventually find practical applications.

Finally, new concepts of fully-polymeric, thin-film batteries have been explored by examining the kinetics of interfaces formed by PEO-based electrolytes and electronically conducting polymers (e.g. polypyrrole) as electrodes. Preliminary results (7) indicate that this type of cell may operate satisfactorily at low rates and at moderately high temperatures.

ACKNOWLEDGEMENTS.

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IONIC CONDUCTION IN POLYOXYETHYLENE RELATED SYSTEMS

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INTRODUCTION

The research to be reported stemmed initially from the pioneering work of Wright and co-workers^{1,2}, and Armand and co-workers³ on alkali metal salt-polyethylene oxide (PEO) complexes. Because of our interaction with those interested in the construction of solid-state batteries, the efforts have been concentrated on lithium salts. In general terms two areas were identified for detailed study

- (1) The elimination or reduction of the mobility of the anion
- (2) A substantial improvement of the overall ionic conductivity.

In pursuit of these objectives, the following aspects were examined, and will be described in sequence

- (1) The effect of salt composition on the ionic conductivity, in particular preparing salts with highly polarisable groups such as fluorine and sulphur. In the first instance salts of monobasic acids were examined with the aim of obtaining high conductivity, but secondly, with the target of inhibiting the mobility of the anion, a lithium salt of a dibasic acid was also included.
- (2) To examine the effect of complete immobility of the anion, blends of poly(ethylene oxide) with lithium salts of anionic polymers were prepared.
- (3) To obtain high ionic conductivity over a wide temperature range, amorphous poly(methoxy polyethylene glycol monomethacrylates) (PEM) were prepared and complexed with lithium trifluoromethane sulphonate $\text{CF}_3\text{SO}_3\text{Li}$. These comb polymers offer an important new range of ionically conducting polymers.

RESULTS AND DISCUSSION

(1) Comparison of different salt complexes⁴

First, results are shown in Figure 1 for PEO complexes with lithium trifluoroacetate CF_3COOLi and lithium trifluoromethane sulphonate $\text{CF}_3\text{SO}_3\text{Li}$. In each case a range of salt concentrations was examined, specified by the ratio of the number of moles of oxygen atoms in PEO to the number of moles of Li^+ -ions (designated as the O/Li^+ ratio). It can be seen that the conductivity values for the $\text{PEO-CF}_3\text{SO}_3\text{Li}$ complexes are about an order of

magnitude higher than those for the PEO- CF_3COOLi complexes. This has been attributed to the greater stability of the trifluoromethane sulphonate anion and a lower degree of ion-pairing, trifluoromethane sulphonic acid being regarded as a very strong monobasic acid. It can be noted that all the conductivity plots, with the exception of the PEO- CF_3COOLi complex with $\text{O/Li}^+ = 4$, show a knee at about 338K corresponding to the crystalline melting of PEO.

Figure 2 shows conductivity results for complexes incorporating the lithium salt of a dibasic acid, dilithium hexafluoroglutarate (LiHFG) $\text{LiOOC}(\text{CF}_2)_3\text{COOLi}$. Comparison with the results of Figure 1 shows that there is a significantly lower value of ionic conductivity than the PEO- CF_3COOLi complexes over the entire temperature range. This is believed to be partly due to the immobilization of the anion in the salt complex formed from the salt of the dibasic acid.

Comparative results were also obtained for the conductivity of PEO complexes with CF_3COOLi , $\text{CF}_3\text{CF}_2\text{COOLi}$ and $\text{CF}_3\text{CF}_2\text{CF}_2\text{COOLi}$ all with $\text{O/Li}^+ = 9$. A systematic decrease in conductivity with increase in anion size was observed.

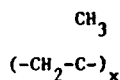
(2) Polymer blends⁴

To obtain a low degree of ion-pairing and hence produce polymer blends with relatively high Li^+ -ion conductivity, salts of anionic polymers derived from strongly acidic polymers were synthesised. The two systems examined were poly(2-sulphoethyl methacrylate-Li salt) (PSEM-Li) and poly(2-(4-carboxyhexafluoro-butanoyl-oxy) ethyl methacrylate-Li salt) (PCHFEM-Li). Results were obtained for the PSEM-Li/PEO blend with $\text{O/Li}^+ = 15$ and the PCHFEM-Li/PEO blend with $\text{O/Li}^+ = 18$. A knee in the conductivity curve was again observed near 338K which corresponds to the melting of the crystalline PEO. The anionic polymer-Li salts will form part of the amorphous phase. The conductivity of the PCHFEM-Li/PEO blend is an order of magnitude greater than that of the PSEM-Li/PEO blend at the same temperature, which may be attributed to the different stabilities of the anions. The conductivities for the PCHFEM-Li/PEO blend are similar to those for the PEO-Li HFG complex but both are somewhat lower than those for the monobasic acid with similar anion stability and identical Li^+ -ion concentration. This result is consistent with the immobilization of the anion in the blend and in the complex from the salt of the dibasic acid.

(3) Comb-like polymers^{5,6}

Recognizing that increased ionic conductivity requires a high amorphous content (note the knee in the conductivity curves observed at the melting point of the crystalline PEO phase) it was decided to examine the behaviour of

amorphous Li-salt complexes. The polymers chosen were poly(methoxy polyethylene glycol monomethacrylates)



with $n=9$ and 22 for PEM 9

and PEM 22 respectively

Results for complexes of these comb polymers with LiSO_3CF_3 (found above to give the highest levels of conductivity in the PEO complexes) are shown in Figure 3. As expected, the knee in the conductivity curve is absent for these amorphous polymers, and the results compare very favourably with the comparable PEO complex ($0/\text{Li}^+ = 18$ in all cases). It is of particular importance that these comb polymers show conductivities in the range 10^{-4} – $10^{-5} \text{ S cm}^{-1}$ at room temperature.

In further work, the influence on the conductivity of increasing the main chain mobility was explored, by obtaining results for polysiloxane comb polymers, complexed with lithium perchlorate LiClO_4 . The polymers are liquids at room temperature but rubbery films can readily be produced by crosslinking. The conductivity results for these systems were similar to those for other fully amorphous poly(ethylene glycol) systems, and showed conductivity values $\sim 10^{-4} \text{ S cm}^{-1}$ at room temperature. Figure 4 shows conductivity plots for two cross-linked films of the siloxane polymers complexed with LiSO_3CF_3 . Very satisfactory values for the conductivity are obtained. For comparative purposes we also prepared lightly cross-linked analogues with the methacrylate backbone polymer. These latter films showed conductivities $\sim 10^{-5} \text{ S cm}^{-1}$ at room temperature 298K and were more thermally stable than the siloxane comb polymers.

CONCLUSIONS

To obtain the most highly conducting polymer electrolytes from polymers containing the oxyethylene repeat unit several key factors have been identified. First, it is desirable to use a wholly amorphous polymer. Secondly it is desirable to retain as much molecular mobility as possible. It has been shown that comb polymers with oxyethylene oligomers as the teeth and methacrylate, acrylate or siloxane backbones satisfy these requirements. Finally, the choice of complexing salt also has to be optimised. Good results have been obtained with lithium trifluoromethane sulphonate.

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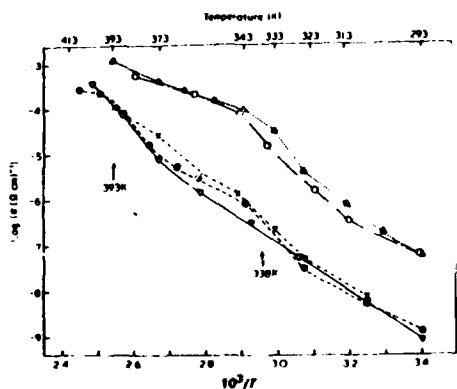


Fig. 1. The logarithms of the conductivities against the reciprocal temperatures for PEO-CF₃COOLi complexes with O/Li = 4 (∇), O/Li = 9 (\circ), O/Li = 18 (\times) and for PEO-CF₃SO₃Li complexes with O/Li = 9 (\blacktriangle), O/Li = 18 (\circ)

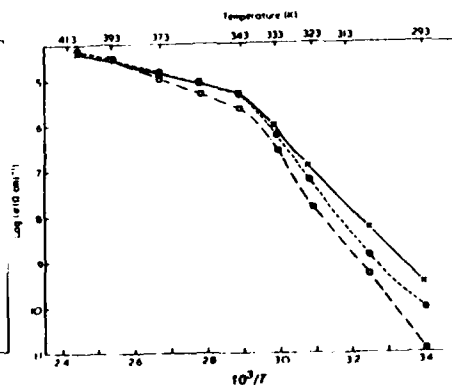


Fig. 2. Log conductivities versus the reciprocal temperatures for PEO-LiNPG complexes with O/Li = 4 (\square), O/Li = 9 (\circ), O/Li = 18 (\times)

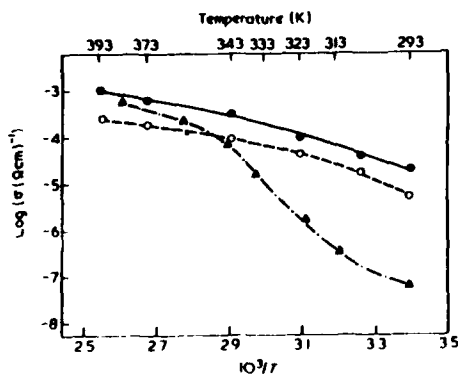


Fig. 3. Log conductivities vs. reciprocal temperatures for the PEM9-LiSO₃CF₃ (\circ), PEM22-LiSO₃CF₃ (\bullet) and PEO-LiSO₃CF₃ (\blacktriangle) complexes O/Li = 18 in all cases

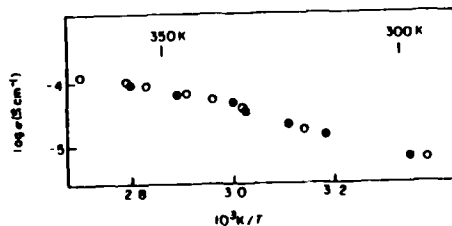


Fig. 4. Conductivity plots for solid crosslinked films of siloxane polymers containing lithium trifluoromethanesulphonate. The side chains are: (\bullet) 50% monomethoxy(polyethylene glycol) 350 and 50% methoxy; (\circ) 25% monomethoxy(polyethylene glycol) 350 and 75% methoxy. In both cases one lithium per 18 $[\text{CH}_2\text{CH}_2\text{O}]$ units

Ionic Conduction of Polymer Electrolytes and Future Applications

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Rubbery state is characteristic of macromolecules. In rubbery state, polymer segments are locally mobile (micro-Brownian motion) like a liquid, whereas long range motion of molecules (macro-Brownian motion) is prohibited by cross-linking structures, such as existence of crystallites and chemically produced network structures. Thus, polymeric materials having physically or chemically cross-linked structures behave like elastic or plastic solids even in rubbery state (above T_g). Certain kinds of polar polymers can dissolve inorganic salts up to a high concentration. In these solid solutions, a part of the dissolved salt is expected to dissociate to ions, as so in liquid electrolyte solutions. Polymer electrolytes with high ionic conductivity, ever obtained, have amorphous and rubbery phases with dissolved salts, and the ionic conduction in these phases is predominant. We summarize here the correlation between structure of polymer electrolytes and their ionic conductivity in terms of carrier transport and generation processes. Our recent study on the application of polymer electrolytes is also presented.

Low molecular weight poly(propylene oxide) (PPO) ($M.W.=10^2-10^3$) is a liquid polymer at room temperature and can dissolve alkali metal salts to form viscous electrolyte solutions. Room temperature ionic conductivity of the electrolyte solutions was $10^{-6}-10^{-5} \text{ Scm}^{-1}$.¹⁾ In the electrolyte solutions, both micro- and macro-Brownian motion of the polymer chain are permitted. If the micro-Brownian motion mediates the transport of ions, solid polymer electrolytes should be obtained. The ionic conductivity of PPO network polymers²⁾ and PPO block copolymers³⁾ containing alkali metal salts reached $10^{-7}-10^{-6} \text{ Scm}^{-1}$. This conductivity was comparable to that of the electrolyte solutions, although in these polymer electrolytes the macro-Brownian motion was frozen. Thus, micro-Brownian motion of polymer segments is primarily the motive force of ionic transport in polymer electrolytes.

The dielectric relaxation time for the backbone motion of PPO

and poly(ethylene oxide) (PEO), which are typical media for polymer electrolytes, is 10^{-9} - 10^{-8} s at room temperature, and its temperature dependence is known to obey the WLF equation. How small ions migrate in these rubbery media is an interesting problem. The temperature dependence of ionic conductivity of amorphous polymer electrolytes also obeys the WLF equation. The change in the conductivity with temperature was similar to that in the dielectric or mechanical relaxation time of backbone motion for the PPO electrolytes, when T_g was used as a reference temperature.⁴⁾ In the PPO electrolytes crosslinked by an azobenzene derivative, the average hole size required to migrate carrier ions was larger than that required for the thermal cis+trans isomerization of the azo-probes.⁵⁾ Fig.1 shows the WLF plots of ionic conductivity for amorphous PEO networks containing 11 different alkali metal salts at the same concentration.⁶⁾ Although the conductivity at a constant temperature differed at most by two orders of magnitude, the WLF plots were represented by one master curve irrespective of the salt species. These results imply that ionic migration does not occur by itself but that the segmental motion with associated carrier ions causes the ionic migration. The moving unit of polymer backbone with associated carrier ions is correlated with that involved in the relaxation process. Since its size is far larger than the volume of naked ions and is nearly constant, independent of the ionic radii, the above phenomena are observed.

Carrier ions in polymer electrolytes, thus, exist as solvated ions by polar groups of polymers. The polymer segments with associated ions constantly rearrange because the polymer electrolytes are in rubbery state. This rearrangement changes the local position of the carrier ions. The solvation of the other segments dominates sometime after the change in the local position of the carrier ions, and the segmental motion causes again the ionic migration. The repetition of the association of the carrier ions to the polymer segments, the segmental motion with associated

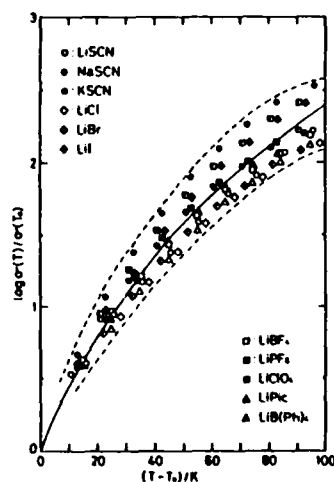


Figure 1 WLF plots of ionic conductivity for PEO-alkali metal salt complexes using a reference temperature $T_g (=T_g + 50^\circ\text{C})$.

ions, and the dissociation from the polymer segments seems to cause the ionic transport in polymer electrolytes. The segmental motion with associated carrier ions is the rate-determining-step for the ionic conduction. The WLF profile of the ionic conductivity with large temperature dependence for transporting small ions is, thus, observed. The ionic mobility in the PPO and PEO network electrolytes was roughly found to be ca. $10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature⁷⁾ by means of the transient ionic current methods.⁸⁾

The ionic conductivity of polymer electrolytes is affected not only by the ionic mobility but also by the number carrier ions. The carrier number is influenced by the incorporated salt species, its concentration, temperature, and polymer structure. The ionic conductivity for the PEO⁶⁾ and PPO²⁾ electrolytes of a constant salt concentration decreased in accordance with the increase in the lattice energies of incorporated salts, when it was compared at the iso-free-volume state. At this state, the increase in the ionic conductivity of the PEO network electrolytes as a function of a salt concentration was smaller than that expected by the complete dissociation.⁹⁾ These results support the conclusion that all of the incorporated salts do not function as carrier ions, and the ion dissociation is suppressed with increasing the lattice energies and concentration of salts. In contrast, the increase in the conductivity of the PPO electrolytes with the salt concentration was larger than that expected by the complete dissociation.⁴⁾ This might be due to the fact that the change in the carrier number with temperature was small in the PEO electrolytes, while that in the PPO electrolytes was not negligible.⁷⁾

For the ion dissociation in polymeric media, solvation of an ion with polar groups in the polymers may be an essential process. There are two possible processes for the solvation in polymeric media; one is the solvation by intrapolymer polar groups and the other is that by interpolymer polar groups. The former process may involve the cooperative interaction of the neighboring polar groups with an ion. When the ionic conductivity of amorphous PEO and PPO electrolytes was compared, the conductivity of the PEO electrolytes was 5-10 times higher than that of the PPO electrolytes, whereas T_g or the ionic mobility of both electrolytes did not differ appreciably one to the other.⁷⁾ The ionic dissociation was, thus, suppressed in the PPO electrolytes. Similar results were obtained in aliphatic polyester electrolytes; the ion dissociation was suppressed in poly(ethylene sebacate), compared with that in poly(ethylene

succinate).¹⁰⁾ We consider that the cooperative interaction of neighboring polar groups with an ion is more important for the carrier generation in polymeric media.

A unique and interesting property of polymer electrolytes, which is not attained by inorganic solid electrolytes, may be the ability to include various

kinds of electroactive molecules in them. The combination of this property with their high ionic conductivity will enable us to use polymer electrolytes as media for electrochemical reactions of electroactive molecules, as we use electrolyte solutions for this purpose. Fig.2 shows schematic view for the electrochemical polymerization of pyrrole using a polymer electrolyte. The electrochemical polymerization produced polypyrrole/polymer electrolyte bilayer composites *in situ*.¹¹⁾ The bilayer composites showed electrochemical activity in solid state. When redox active molecules, such as ferrocene, were incorporated in polymer electrolytes, the molecules underwent redox reactions in response to the potential of an electrode. The future application of polymer electrolytes will open in the fields; they are used as a medium of ions and molecules which response to electrode potentials.

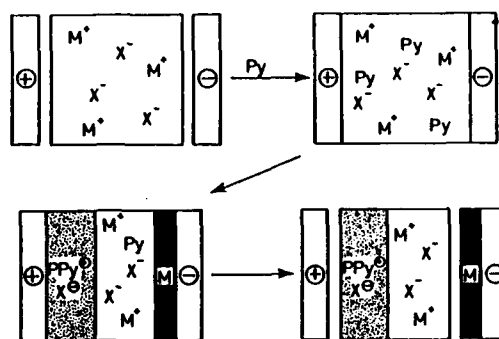


Fig. 2 Schematic view for electrochemical polymerization of pyrrole using ion-conducting polymers as a solid electrolyte.

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ASPECTS OF SOME CRYSTALLINE COMPLEXES OF
POLY(ETHYLENE OXIDE) WITH ALKALI IONS

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ABSTRACT

Poly(ethylene oxide) (PEO) has become well-known as a medium for ionic conduction of inorganic alkali ion salts. This process takes place predominately through the amorphous regions of the PEO-alkali salt complexes.

However, PEO alkali ion complexes may be highly organised and we have recently begun to explore the possibilities of using PEO to carry structured arrays of electroactive or optically active species including those which incorporate aromatic rings. Such structural information that is presently available^{1,2,3} suggests that PEO-Na⁺ and PEO-Li⁺ crystalline phases have stoichiometries of 3 mol of EO unit per 1 mol of cation and two molecular units of complex extend over the fibre repeat distances which range from 7.2Å to 8.4Å. Thus, the positive centres may be distributed along the chain with adjustable spacing ca. 3.6Å - 4.2Å that should comfortably accommodate stacks of charged aromatic rings. Accordingly, complexes of PEO with a variety of organic acid salts and charge transfer salts have been prepared^{4,5,6}. The former display lyotropic and thermotropic behaviour while the latter form flexible, electronically conducting films. The preparation, structure and properties of these materials will be discussed.

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RECENT RESULTS ON A 10 Wh CELL BASED ON PEO-LiClO₄
ELECTROLYTE AND PRELIMINARY DATA ON NEW SALT-POLYMER
COMBINATION FOR IMPROVED PERFORMANCES.

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INTRODUCTION

The ACEP project (Accumulateurs à Electrolyte Polymère) has been going on at IREQ since the early eighties following an original approach suggested by M. Armand of the University of Grenoble, France (1).

These all solid-state batteries use polymer electrolytes made of chain having functional groups that can easily dissolve the lithium salts and confer pure ionic (ideally cationic) conductivity on the electrolyte. Polyether is by far the best known family of polymers that have been tested for battery applications.

Over the years many improvements have been made in the polyether-based electrolytes, both from the point of view of the polymer chain itself and the type and nature of salts dissolved in the polymer network.

The following results on the 10 Wh demo-cells reveal in practical terms the limits of a particular choice of components and their physical arrangements.

Some new results obtained for mid-temperature applications (60°C) will be presented as a demonstration of improved performance associated with the electrolyte and the optimization of lithium electrodes.

10 Wh DEMO-CELL AT 100°C

The first results on a 10 Wh demo-cell were presented in Kyoto, Japan during the "Third International Meeting on Lithium Batteries" in May 1986 (2).

The cell consists of twelve (12) groups of 4x1-cells stacked into a prismatic stainless steel casing on which individual feedthrough connectors were provided. The assembly of the cells was achieved by hot-pressing together the cell components. Preliminary results showed that no scale effect was encountered going from 4 cm² laboratory cells to the 4800 cm² demo-cell. Some parallel and series behavior cases were also briefly described.

In the present paper, we describe in more details the follow-up of the cycling of this demo-cell. Figure 1 shows the cycling profile of one group of 4x1-cells as recorded over a period exceeding a year. As shown, cycling was performed at different discharge rates (C/100 to C/1) at 95°C in various series and parallel configurations. An "aging" process started after the demo-cell was tested in series arrangement (c.a. ~150th cycle) that affected the power characteristics of the whole cell. Nevertheless, cycling was resumed and followed by a six-month period of complete inactivity at 95°C. No self-discharge was noticed during this rest period: open circuit voltages (OCV) starting at 2.56 ± 0.02 V and ending at an average of 2.52 ± 0.02 V.

Afterwards, for an all-parallel configuration, the total capacity of the demo-cell was still available but at low discharge rates (C/100).

SERIES CYCLING

8.2

The importance of cell equalization became obvious when series cycling tests were performed on the demo-cell. At that time, the reproducibility of the positive electrode surface capacity was of the order of $\pm 5\%$ (doctor blade slurry technique) which proved to be quite insufficient for continuous series cycling.

Cells were linked two by two in parallel and then in series of three as shown in Figure 2. The figure shows the discharge curves at C/4 for individual groups of the series along with the total series (right scale). Rapidly, because of unbalanced capacities:

group 1- 2548 C for U= 75.0 % |
group 2- 2491 C for U= 73.9 % | starting capacities
group 3- 2448 C for U= 72.4 % |

and for an overall inverting voltage of 4.5 V for the discharge state, the groups do not invert at the same individual voltages. From the 4th cycle:

	group 1	group 2	group 3
cyc.#4	1.75 V	1.48 V	1.30 V.
cyc.#5	1.75 V	1.52 V	1.18 V.
cyc.#6	1.80 V	1.62 V	1.08 V.

The last value of 1.08 V is much too low for the positive electrode and causes some degradation of the material. While the weaker link of the series becomes over-polarized, the two other groups reach voltages that correspond only to shallow discharges. As the cycling progresses things get worse since the performances of the weaker cell continue to decrease.

However, series cycling proved to be quite viable if good cell balancing is achieved during electrode preparation processes. For example, when cells have positive electrode capacities that do not spread over by more than 1 %, we have reached more than 40 cycles without experiencing any deteriorous single cell overvoltages.

THERMAL MANAGEMENT INFORMATION

For high power applications, e.g. traction type batteries for E.V. applications, the understanding of heat effects assumes a particular importance. As a matter of fact, the mechanism of heat generation inside the battery during cycling and the way heat may be dissipated need to be well understood in order to prevent any temperature excursions that would otherwise damage the whole cell. It is essential, for example, that nowhere in the cell the melt temperature of the electrolyte be reached and cause swelling of the various constituents. In the same way, for kinetic reasons, the higher the temperature, the more severe the degradation of components and the corrosion problems involving current collectors.

To get a first glance of heat effects inside ACEP type batteries, we have introduced three small thermocouples distributed in-between the 12 groups of 4xBI-cells along the middle axis. The outputs of these thermocouples were recorded simultaneously along with cell data during cycling. Figure 3 shows a typical temperature profile encountered during a 2 A (C/1) discharge cycle.

The temperature increases given in Figure 3 demonstrate that in most probable situations even at very high discharge rates there would not be any serious damage to the cell due to temperature excursions for this particular configuration.

LITHIUM CYCLING AND OPTIMIZATION

The lithium foil used in the construction of practical cells has to be optimized for many reasons: first, the battery grade lithium is an expensive material and its consumption must be kept as low as possible. It is also difficult to produce

8.3

at very thin levels, i.e. at less than 100 microns where lamination takes over the direct extrusion processes. The other factor relates to the fact that any excess of lithium represents an important penalty particularly as to the volume energy content. For example, for a positive electrode having a 5 C/cm^2 surface capacity, only 8 microns of lithium are stoichiometrically needed; thus using a 150 microns commercial lithium would represent an important waste of costly material.

In the present studies, two types of lithium were tested:

- thin lithium foil supported on a metallic current collector
- unsupported lithium foil for use in bi-cells.

The tests were performed on small cells of 4 cm^2 areas. The data on lithium performances was characterized by F.O.M. values which are given by:

$$\text{F.O.M.} = \frac{\# \text{ cycles} \times \text{average capacity}}{\text{available lithium}}$$

Different lithium excesses were calculated depending on positive electrode capacity and lithium thickness. Lithium was further laminated in laboratory from readily available commercial battery grade lithium. (Foote or Lithcoa).

For bi-cells using unsupported lithium, F.O.M. of 50 have been obtained (with 3 excesses) at around the 170th cycle.

For copper supported lithium, F.O.M. of nearly 100 were reached for a 2 excesses Li foil (13 microns) at the 320th cycle.

The electrolytes used were modified PEO-based polymers and LiClO_4 in a 20:1 ratio. The cells were cycled at 60°C a C/4 discharge rate and C/8 charge regime. Deep discharges were achieved in each cycle at voltage limits of 1.5 to 3.3 volts.

IMPROVED ELECTROLYTES FOR BETTER CELL PERFORMANCES.

High temperature studies (100°C) have shown that POE-based electrolytes suffer two major problems which are:

- a) Low material utilizations and lithium dendrite growth when the positive surface capacities exceed 8 to 10 C/cm^2 .
- b) Inefficient lithium rechargeability and dendrite growth when cells are operated at temperatures lower than 70°C.

These particular limitations are to be imputable to the high crystallinity content of many POE-based electrolytes and to their relatively poor adhesive properties which hinder the formation of good interfaces. Many of these disadvantages have been solved in part or totally by modifications to the polymer and to the lithium salts. A good example of this is shown in Figure 4 in which a modified POE-based electrolyte has been used in cycling a VO_x/Li cell at 96°C. High and stable utilizations are obtained with this electrolyte for over 150 cycles.

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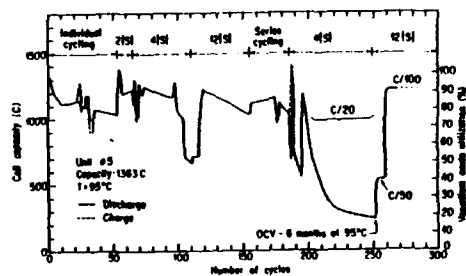


Figure 1. Typical cycling profile of one the 4x1-cell group obtained for various series and parallel configurations of the 10 Wh demo-cell.

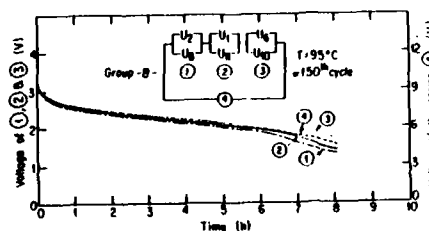


Figure 2. Discharge curves obtained during series cycling of six (6) 4x1-cell groups connected in a 10 V series arrangement.

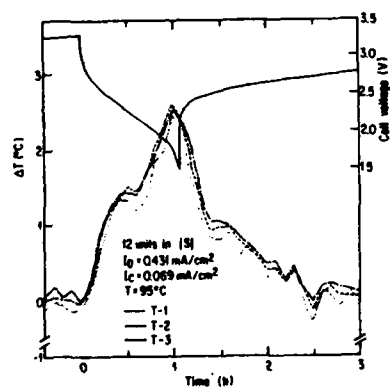


Figure 3. Temperature increases recorded with three thermocouples embedded inside the 10 Wh demo-cell during a discharge performed at a C/1 regime.

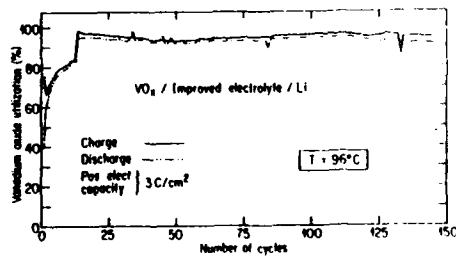


Figure 4. Typical cycling profile obtained for a VO_2/Li cell using a modified POE-based improved electrolyte. Voltage limits 1.5 and 3.3 V

A POLYMERIC ELECTROLYTE RECHARGEABLE LITHIUM BATTERY

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Complexes of poly(ethylene oxide), PEO, and lithium salts (e.g. LiCF_3SO_3 or LiClO_4) are promising materials as advanced, solid-state polymeric electrolytes for the development of high-energy, lithium batteries (1-4).

In this work we describe the characteristics and the performance of one type of such battery, based on the $\text{Li}/\text{Li}_{1+x}\text{V}_3\text{O}_8$ electrodic couple.

Figure 1 shows the potential composition curve of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ obtained at 100°C by intercalation (discharge) and deintercalation (charge) galvanostatic steps in a cell using the $(\text{PEO})_9\text{LiCF}_3\text{SO}_3$ electrolyte. A single-phase behaviour, typical of solid-solution formation, is only visible up to an x value of about 1.5. At higher Li^+ content, a structural rearrangement of the vanadium bronze takes place; a new phase appears which is in equilibrium with that corresponding to the upper limit of the solid solution (5-7) and thus the potential tends to remain constant as it is typical of a two-phase region. Detailed x-ray analysis (5-7) has shown that these changes in structure are highly reversible and thus the vanadium bronze electrode can be repeatedly cycled over a composition range of $0 < x < 3$. This is confirmed by the matching between the potential values obtained in discharge and those found in recharge (Figure 1).

Figure 2 shows the cycling behaviour of a lithium-vanadium bronze battery using the $(\text{PEO})_9\text{LiClO}_4$ electrolyte. The capacity decline with cycle number has a trend often observed in polymer electrolyte batteries, as typically reported with systems using the V_6O_{13} cathode material (8-9) and the same $\text{Li}_{1+x}\text{V}_3\text{O}_8$ material assembled and tested in another laboratory (9). This trend is not connected with an irreversible alterations of the structure of the $\text{Li}_{1+x}\text{V}_3\text{O}_8$ vanadium bronze but rather with macroscopic factors, such as deformations and contact losses. Determination of the

design is therefore critical in this cell and probably in the generality of polymer electrolyte systems.

ACKNOWLEDGEMENTS

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POLY(ETHYLENE OXIDE)- $\text{Cu}(\text{CF}_3\text{SO}_3)_2$
POLYMER ELECTROLYTE

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A continuously growing interest is devoted to polymer electrolytes because of their specific advantages, such as plasticity and ease of preparation in the form of thin films. The majority of the studies have been so far focussed on complexes between poly(ethylene oxide), PEO, and lithium salts, which may find application as polymer electrolytes in versatile, high-energy batteries.

However, ionically conducting polymers appear now to be of importance not only in the battery field but also, and perhaps even more specifically, in electrochemical displays and sensors. For this type of application, the use of polymer complexes based on salts of metals less reactive than lithium may be advantageous. Considering that the above devices are generally directed to the consumer market, electrolytes based on common, low-cost metal ions would be highly desirable.

Here we describe the characteristics of new copper polymer electrolytes formed by the combination of poly(ethylene oxide) and copper trifluoromethanesulfonate, $(\text{PEO})_x\text{Cu}(\text{CF}_3\text{SO}_3)_2$, at various molar ratios of salt to polymer repeat unit.

Figure 1 shows that the conductivity of a typical example of these electrolytes, i.e. the $(\text{PEO})_9\text{Cu}(\text{CF}_3\text{SO}_3)_2$ complex, has a reproducible behaviour in the heating and cooling run, with a curvature which is typical of amorphous PEO-based conductors. It is worth noting that the total conductivity of the complex is quite high, reaching values of the order of $10^{-4} (\text{ohm cm})^{-1}$ around 100°C .

By d.c. measurements under blocking conditions, the electronic contribution to the total conductivity has been evaluated and also reported in Figure 1. The difference between the total and the electronic conductivity, which may be considered as the pure ionic conductivity of the polymer electrolyte, increases as temperature increases, to become greater than two orders of magnitude at about 100°C .

Finally, d.c. polarisation studies suggest that copper ions are the main ionic carriers and thus that the $(\text{PEO})_x\text{Cu}(\text{CF}_3\text{SO}_2)_2$ complexes may indeed be considered as new polymer copper ion conductors.

RADIOTRACER SELF-DIFFUSION MEASUREMENTS IN POLYETHYLENE OXIDE
AND POLYPROPYLENE OXIDE ELECTROLYTES .

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INTRODUCTION

Since the early work [1,2] on the polymer electrolytes formed between polyethylene oxide (PEO) and alkali metal salts (MX) experimental investigations of ion transport have predominantly utilized electrical conductivity measurements. Recently, direct studies of the diffusion of ions in these materials have been reported [3] using radiotracer or nuclear magnetic resonance techniques. Most of the work has centred on MX.PEO complexes and a major conclusion is that both cations and anions are mobile in these materials. In this contribution we will report the results of radiotracer diffusion measurements for the ions in complexes between NaSCN and PEO and between NaSCN and polypropylene oxide (PPO). The objective of the work is to establish the transport number of the ions and to obtain information on the diffusion mechanism by correlating diffusion, D , and ionic conductivity, σ , results.

In a tracer experiment the labelled ions are distinguishable and correlations between successive diffusive steps must be considered. Thus the tracer diffusion coefficient, D^* , is related to the 'random' D via

$$D = fD^* \quad (1)$$

where f is the correlation factor. The magnitude of f contains information on the diffusion mechanism [4] and can be determined experimentally from measurement of σ and D^* i.e. from

$$\frac{\sigma}{D^*} = \frac{Nq^2f}{kT} \quad (2)$$

We have reported [5] $^{22}\text{Na}^+$ and $^{14}\text{CN}^-$ diffusion in NaSCN.PEO₈ and we will present new results for NaSCN.PEO_x with $x = 6$ and 12. Complexes of alkali metal salts with PPO are amorphous at all temperatures. We have made the first direct diffusion measurements in PPO complexes and will present $^{22}\text{Na}^+$ and $^{14}\text{CN}^-$ diffusion measurements in NaSCN.PPO₈.

EXPERIMENTAL

PEO (molecular weight 5×10^6) was obtained from BDH Ltd. The PPO was obtained from Hercules Incorporated in the form of PAREL 58 elastomer. Films of NaSCN.PEO_x were prepared by casting from a solution of the components in acetonitrile or methanol (BDH Analar grades). In order to obtain samples thick enough for diffusion studies (~ 3 mm thick) the casting procedure had to be repeated several times. Films of NaSCN.PPO_8 were prepared in a similar manner. However, an improved method of preparing diffusion samples of this material was developed which involved pressing small pieces of pre-cast film in a Teflon die at 400K under vacuum. The conductivity of cast and pressed films were the same.

Diffusion samples (5 to 15 mm diameter \times ~ 3 mm thick) were affixed to stainless steel mounts with epoxy resin. The top surfaces were microtomed flat and radiotracers, ^{22}Na and S^{14}CN (Amersham Ltd), were applied by painting on a solution of the salt in an organic solvent. The diffusion couples were annealed under vacuum for known times at fixed temperatures. After the anneal thin sections, 20 or 40 μm , were microtomed from the surface and the activity in each section assayed by liquid scintillation counting. The sectioning of the PPO samples was performed by cooling the samples on a specially developed cold-stage for the microtome. Diffusion coefficients were evaluated from plots of $\log(\text{activity})$ versus $(\text{penetration depth})^2$ [5].

Additional conductivity measurements were taken with a Wayne-Kerr B221 bridge operated at 50kHz.

RESULTS

A detailed discussion of the diffusion profiles in NaSCN.PEO_8 has already been reported [5]. The profiles for all the NaSCN.PEO_x were similar for all compositions. The interest is in the high conductivity region above 340K and the results in this region were fitted to the Arrhenius equation,

$$D^* = D_0^* \exp -Q/kT \quad (3)$$

Here D_0^* and Q are the pre-exponential factor and activation energy, respectively. The results of those fits are given in Table 1. It is worth noting that the SCN^- ion is more mobile than the Na^+ ion at all temperatures and in all samples. In addition, D^* for each ion shows little dependence on composition.

Good profiles were obtained for ^{22}Na and S^{14}CN diffusion in NaSCN.PPO_8 and the Arrhenius parameters are given in Table 1. In the temperature range studied $D^{\#}$ was virtually the same for both ions.

TABLE 1
Radiotracer Diffusion Data for NaSCN.PEO_x and NaSCN.PPO_8

	^{22}Na		S^{14}CN	
	$D_0/\text{m}^2\text{s}^{-1}$	Q/kJmol^{-1}	$D_0/\text{m}^2\text{s}^{-1}$	Q/kJmol^{-1}
NaSCN.PEO_6 T=340 to 430K	1.7×10^{-8}	25 ± 6	6.5×10^{-7}	35 ± 10
NaSCN.PEO_8 " " "	7.7×10^{-7}	36 ± 2	1.0×10^{-7}	29 ± 5
NaSCN.PEO_{12} " " "	8.0×10^{-7}	36 ± 3	2.3×10^{-7}	30 ± 5
NaSCN.PPO_8 T=330 to 430K	1.6×10^{-2}	75 ± 5	1.3×10^{-2}	74 ± 6

DISCUSSION

The objective of this work is to compare the diffusion and the conductivity in these materials. For the PEO films this is complicated by the fact that the samples contain crystalline and amorphous regions. The values of $D^{\#}$ only reflect motion in the amorphous regions. The conductivity in the amorphous region has been evaluated using the phase diagram determined from differential scanning calorimeter measurements[6]. This was used to calculate a "conductivity" diffusion coefficient, D_0 , via equation (1) using $f = 1$. In this calculation N for the amorphous phase was also evaluated from the phase diagram. Thus there are relatively large uncertainties in the calculation, particularly for films with a high salt concentration. The comparison of D_0 and the total $D^{\#}$, $D_t^{\#}$, (defined as $D_t^{\#} = D_{\text{Na}}^{\#} + D_{\text{SCN}}^{\#}$) for NaSCN.PEO_x , with $x = 8$ and 12 are shown in Figure 1. At the highest temperatures, in both systems, $D_t^{\#}$ is very close to D_0 suggesting $f \sim 1$. At lower temperatures $D_t^{\#} > D_0$ and there are two possible explanations. Firstly, the diffusion may contain a contribution from the motion of uncharged species, e.g. ion pairs, which do not contribute to σ . Secondly, the discrepancy may reflect uncertainties in the evaluation of D_0 . Unfortunately, the smaller discrepancy in NaSCN.PEO_8 fits both explanations, although we tend to favour the latter of the two.

The fully amorphous nature of NaSCN.PPO_8 makes for a simpler evaluation of D_0 and its comparison with $D_t^{\#}$. The comparison is shown in Figure 2. In this

case $D_t^* > D_0$, however, the discrepancy is only just outside the experimental error. The activation energies for the two measurements are virtually identical.

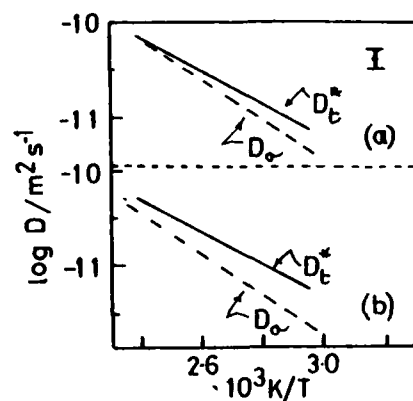


FIGURE 1

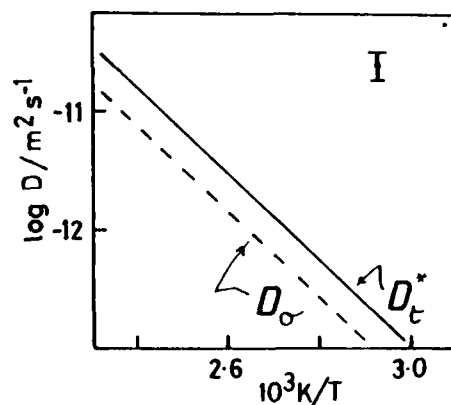
(a) NaSCN.PEO₁₂ (b) NaSCN.PEO₈[the error bars represent the error estimate on D_t^*]

FIGURE 2

NaSCN.PPO₈

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PRELIMINARY RESULTS ON A NEW POLYMER ELECTROLYTE,
 $\text{Hg}(\text{ClO}_4)_2$: POLY(ETHYLENE OXIDE)

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Recent years have witnessed a growing interest in the preparation and characterisation of solid polymer electrolytes containing salts with divalent cations.^{1,2,3} In some cases both ions appear to be mobile while in others only one ionic species supports conduction. Divalent mercury compounds, eg. HgCl_2 ,⁴ have been incorporated into a polymer matrix, however they exist as discrete molecules within the polymer. To our knowledge ionic mercury(II) salts have not been introduced into solid polymers. Here we present some preliminary results on a new polymeric electrolyte, $\text{Hg}(\text{ClO}_4)_2$: poly(ethylene oxide).

*On leave from The Institute of Physics, Warsaw Technical University, Poland.

Film Preparation

All operations were carried out in a high integrity argon filled glove box. Films were prepared by solvent casting from acetonitrile; the acetonitrile (Aldrich, 99%, gold label) was used without further purification. $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Alfa, > 99%) was first dissolved in acetonitrile and the resulting solution dried by adding an excess of freshly activated molecular sieve. Comparison of the IR spectra for this solution before and after addition of the molecular sieve with that of pure, rigorously dried, acetonitrile confirmed that the water of crystallisation had been removed, at least within the resolution of the IR technique. Poly(ethylene oxide) (BDH, m.wt. 5 million) was dried at 50°C under vacuum for 48 hours prior to use. Appropriate quantities of this polymer were added to the mercury perchlorate in acetonitrile after removing the molecular sieve, the resulting solution was stirred continuously for 24 hours. Films were then cast on a teflon plate or mercury surface, with the solvent being allowed to evaporate slowly at room temperature. Near-transparent films, typically 50-200 μm thick, were obtained by this method. No evidence for the presence of acetonitrile or H_2O was observed in the infra-red spectra of these films.

Only one electrolyte composition, $(\text{PEO})_{20} \text{Hg}(\text{ClO}_4)_2$ is discussed in this abstract, results for additional compositions will be presented at the conference.

Phase Identification

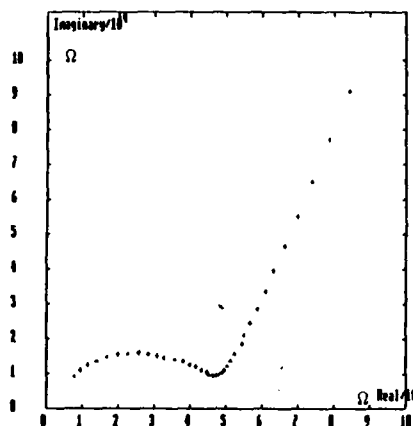
Powder X-ray diffraction patterns of the 20:1 electrolyte indicated that the films were amorphous to X-rays. If crystals do exist they must be of very small dimensions.

Electrical Characterisation

The polymer electrolyte conductivity was determined by ac impedance measurements using a two electrode technique. The electrolyte films was supported in a teflon bodied cell between

two mercury filled reservoirs, each mercury pool was in turn in contact with stainless steel cylinders that facilitated electrical connection to the impedance equipment. The entire cell was assembled within the glove box and inserted into a gas-tight pyrex chamber with screened electrical breakthroughs; this permitted removal of the cell from the glove box for subsequent impedance measurements. Temperature control was achieved by mounting the pyrex cell inside a non-inductively wound tube furnace controlled to $\pm 1^\circ\text{C}$.

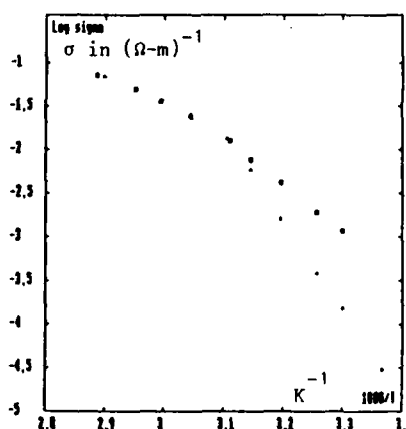
Fig. 1 Complex impedance plot for the two electrode cell $\text{Hg}/(\text{PEO})_{20}\text{Hg}(\text{ClO}_4)_2/\text{Hg}$ at 35°C . The impedance has not been corrected for the cell dimensions.



A.C. impedance data were collected using a Solartron 1250 and 1286 Electrochemical Interface. A typical complex impedance plot is shown in Fig. 1; the semicircle at high frequencies is associated with the bulk electrolyte impedance, the dc conductivity may be estimated from the low frequency intercept on the real axis. The low frequency spike is indicative of blocking electrode behaviour, this suggests that the ionic conductivity is largely due to the migration of perchlorate anions with the mercury ions remaining essentially fixed in the polymer matrix. The temperature dependence of the electrolyte conductivity is shown in Fig. 2. On heating (data points indicated by crosses on Fig. 2) two regions are observed; at low temperatures

the plot is linear with an activation energy of 2.0 eV, at high temperatures the plot appears to be curved, however more data points are required to confirm this curvature. On cooling (open boxes indicate those points obtained on cooling) significant hysteresis is observed below the transition temperature, at these lower temperatures the conductivity slowly falls to the value observed on heating.

Fig. 2 Log σ against $1000/T$ for the 20:1 electrolyte, + = heating cycle, \square =cooling cycle.



Conclusions

A new polymer electrolyte $\text{Hg}(\text{ClO}_4)_2$: poly(ethylene oxide) has been prepared and preliminary characterisation carried out. Measurements suggest that the electrolyte is a perchlorate ion conductor. The temperature dependent conductivity of the 20:1 composition exhibits a linear Arrhenius region at low temperatures and is apparently curved at high temperatures.

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ION MIGRATION IN LIQUID POLYMER ELECTROLYTES

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In viscoelastic films of poly(ethylene oxide) (PEO) and other polymer solvents containing dissolved salts, such as LiClO_4 , LiCNS and NaCNS , it is now accepted that ion migration involves liquid-like motions of ions and polymer segments [1,2]. This viewpoint is consistent with the adherence of transport properties (notably the conductivity) to the well-known Vogel-Tamman-Fulcher equation where $\sigma = A \exp[-B/(T - T_0)]$ where T_0 is the zero mobility temperature (somewhat lower than T_g) [3].

Outstanding questions concern: (i) the extent of ionic dissociation in these polymer solvents, and (ii) the nature of mobile species (i.e. the share of the total current carried by the anions and cations, respectively). To address these issues we have investigated the behaviour of solutions of Li, Na and K thiocyanates in liquid polymers which are low molecular weight (non-crystallisable) copolymers of ethylene oxide (EO) and propylene oxide (PO) [4].

Fig. (1) shows the dependence of molar conductivity, Λ , on \sqrt{c} for LiCNS , NaCNS and KCNS at 55°C [5]. There is a well defined pattern of conductivity minima and maxima providing strong indications of ion association and ion redissociation effects.

We account for these trends (and other observations, see below) in terms of a very simple model, Fig. (2). The key features of this are:

(i) the strong intramolecular solvation of cations by oxygens in the polyether chains, (ii) concentration dependent ion association, (iii) the relative mobility of the anions, and (iv) the ability of these mobile ions to act as

transient crosslinks through electrostatic interactions with Li^+ ions solvated by neighbouring polymer chains.

We see in Fig. (2)(a) a situation where ion association effects predominate at low concentrations, and the conductivity minimum is observed. In Fig. (2)(b), we see redissociation occurring at higher concentrations. This latter effect accounts, clearly, for the rise in Λ , but also for its subsequent decline as "crosslinking" effects lead to reduced segmental mobility, and ion drag effects become more important.

This model has important (and largely discouraging) implications for the operation of Li-polymer batteries at low (i.e. ambient) temperatures. It implies that most of the current is carried by the anions, and that t_{Li^+} is very small.

This conclusion is confirmed by transport number determinations using the classical Hittorf technique with cells of the type:



The value of t_{CNS^-} is determined by chemical analysis. Typically values of t_{CNS^-} are 0.90 or greater - consistent with the model proposed, and also some literature values, e.g. ref. [6].

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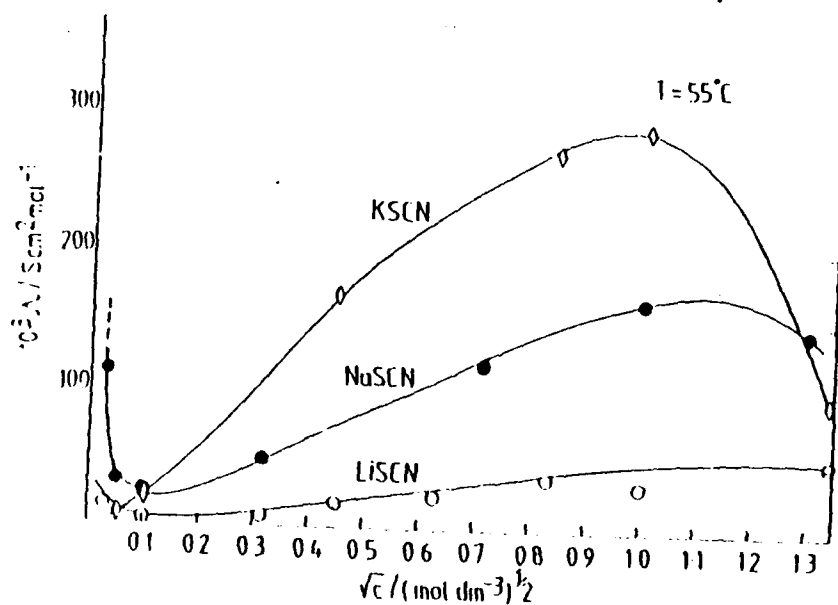


Fig. (1) Molar conductivity Λ versus \sqrt{c} for solutions of LiSCN, NaSCN and KSCN in PO/EO copolymer at 55°C .

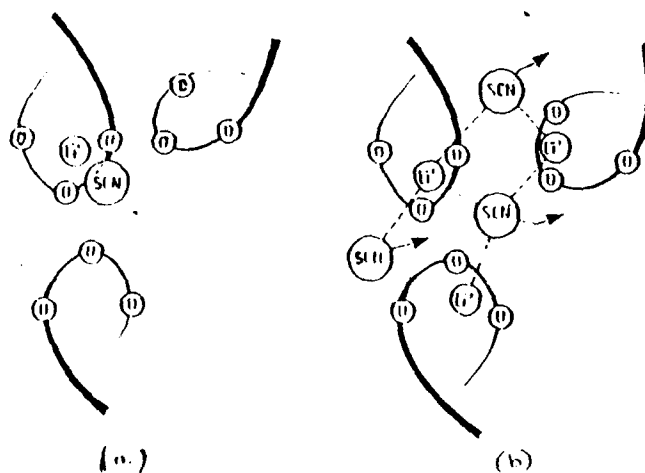


Fig. (2) Solvation in liquid polymers:
 (a) Ion pair formation in dilute solutions.
 (b) Redissociation effect and transient crosslinking in concentrated solutions.

SOLID POLYMER ELECTROLYTES WITH STABLE ELECTROCHEMICAL PROPERTIES

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In a previous paper [1], we have described a composite solid polymer electrolyte able to keep its electrochemical properties upon a long term storage. In addition to the basic polyethyleneoxide (PEO)-lithium salt system, our material includes an elastomer poly(butadiene-co-acrylonitrile) and a styrenic macromonomer of PEO (SEO). A thermal treatment of the whole system causes a radical crosslinking process, which pins the amorphous phase at low temperature. A primary battery with Li/MnO₂ electrodes was stored 1670 days with no change in the resistance for the last 1400 days and keeping half of its initial capacity.

This paper is dealing with some data obtained from a.c conductivity and W.A.X.S measurements in order to get a better understanding of the effect of the macromonomer on the electrochemical properties.

The solid electrolytes were obtained by casting a solution of the different constituents (PEO, macromonomer, elastomer and LiCF₃SO₃) in acetonitrile. In the following, the ratio PEO/SEO (w/w) will be used to reference the samples. Those were then heated at 150°C during one night and then stored at room temperature under an argon atmosphere.

The temperature dependence of the ionic conductivities were obtained from ac impedance measurements over a frequency range between 0.1 Hz and 65 kHz, using a 2020 button cell in which the electrolyte was packed between either two Li or Ni electrodes of the same diameter, with decreasing temperatures from 100°C to room temperature.

X-ray diffraction was carried out by exposing the samples to nickel-filtered CuK α radiation at ambient temperature for 200 seconds. The intensity of the diffraction lines was plotted vs. the diffraction angles θ from 5° to 15°.

Fig.1 displays the temperature dependence of the conductivity for electrolytes having various macromonomer concentration by using a cell with blocking electrodes (Ni). The same bulk

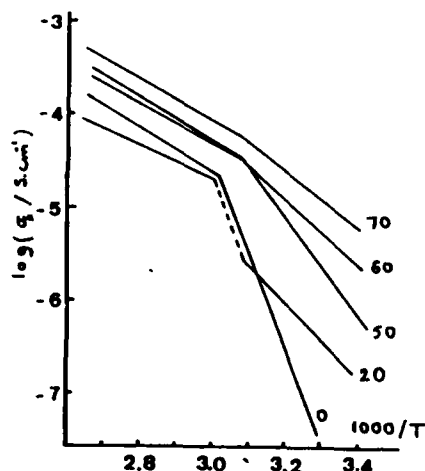


Fig 1. Temperature dependence of bulk conductivity for eletrolytes having various proportions of SEO.

resistances were also obtained with cells having two non-blocking Li electrodes allowing the measurements of both bulk and transfer resistances. This behaviour can be described by an Arrhenius-type relation valid for each of the two temperature ranges. The conductivity was found to increase with the macromonomer proportion and a value of 10^{-8} S.cm $^{-1}$ at room temperature was measured with the 40/60 electrolyte.

The activation energy E_a of the ion conduction mechanism is a decreasing linear function of the macromonomer concentration (except for the 80/20 electrolyte) from 2.1 to 0.5 eV for the temperatures below the transition temperature between the two segments. At higher temperatures, E_a is staying at a constant value around 0.44 eV.

The discontinuity at the transition temperature for the 80/20 electrolyte has to be pointed out. Such a feature was observed by Robitaille [2] with the PEO-LiCF $_3$ SO $_3$ system in all the composition range and the corresponding temperature was attributed to the eutectic melting temperature. This electrolyte displays also an important discontinuity when measuring the E_a values, lower than the other ones.

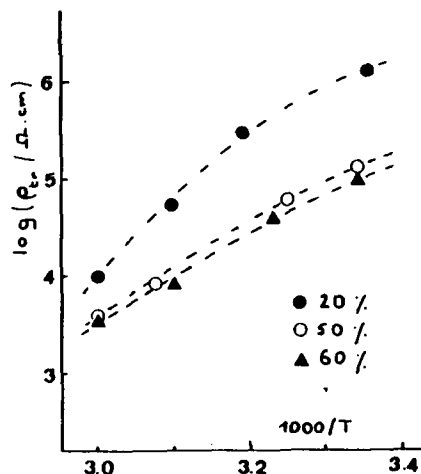


Fig 2. Temperature dependence of transfer resistivity for three kinds of electrolytes.

The temperature dependence of the transfer resistances is shown in Fig 2. Once again is underlined the difference between the 80/20 electrolyte and the other ones. The two latter are displaying almost the same values lower than the first one. It is noteworthy that the three electrolytes cannot be described by a VTF equation.

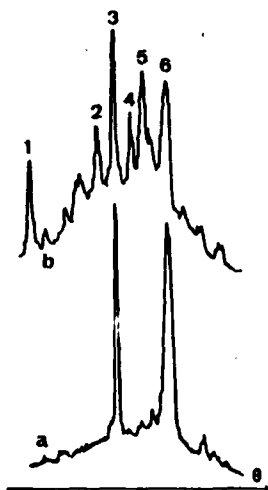


Fig 3. Diffraction patterns of PEO/elastomer/SEO without (a) and with (b) lithium salt.

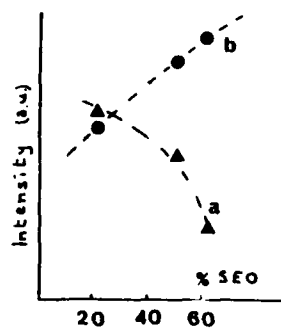


Fig 4. Intensity of various diffraction lines related to non-complexed (a) and complexed (b) PEO.

Fig.3 is showing two diffraction patterns, without and with the lithium salt. The assignments of the diffraction lines were made in reference to those of the PEO and PEO-LiCF₃SO₃, as described previously [2,3]. The lines 3 and 6 ($2\theta = 0.334$ and 0.409 rad) were attributed to the crystallized PEO in a monoclinic unit cell. The addition of the salt produced the new lines 1,2,4 and 5.

The measurements of the Bragg angle values at room temperature show that the addition of the elastomer and the macromonomer does not alter the monoclinic unit cell of the crystallized PEO (Fig 3a). As a consequence, the macromonomer seems not to make a solid solution with the crystallized PEO and to be staying in the amorphous phase. When adding the salt, no new diffraction lines appeared, as compared to the diffraction pattern of the simple PEO-salt system. Nevertheless, the intensity of the diffraction lines of the non-complexed crystallized PEO is decreasing when adding the macromonomer while those of the complexes are increasing (Fig.4). This result could be explained by assuming first that the macromonomer acts as a diluent of the PEO, restricting its crystallization and second that the lithium salt is preferentially complexed with the macromonomer ethoxy units giving small crystallites allowing easy exchange with the amorphous phase and then not disturbing too much the conduction mechanism.

Aknowledgements: The authors are indepted to C.G.E. for financial support and to Mrs. A. de Guibert, Dr. J.F. Fauvarque and X. Andrieu for helpful discussions and technical assistance.

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AMINOSIL, A NEW ORGANOSILICATE GLASS SOLID PROTONIC CONDUCTOR

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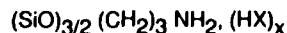
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Aminosils are new solid protonic electrolytes obtained by sol-gel process, by dissolving an acid in a solid material. The starting material is an organically modified silicate which gives, after hydrolysis and condensation, an organic-inorganic glass.

The silica network gives good mechanical resistance and "good" thermal stability. The organic radicals solvate the acids. For that reason alkoxysilane carrying a strong basic radical like $-(CH_3)_2NH_2$ have been chosen.

The chemical formula of aminosil is then :



with a molecular mass around 3 000 and a density of 1.3.

The conductivity was studied as a function of the nature of the acid, its concentration and with variable temperature. The best conductivity ($10^{-3} \Omega^{-1}cm^{-1}$ at $120^\circ C$) is given by : $x = 0.1$ for $HX = HCF_3SO_3$

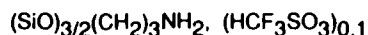
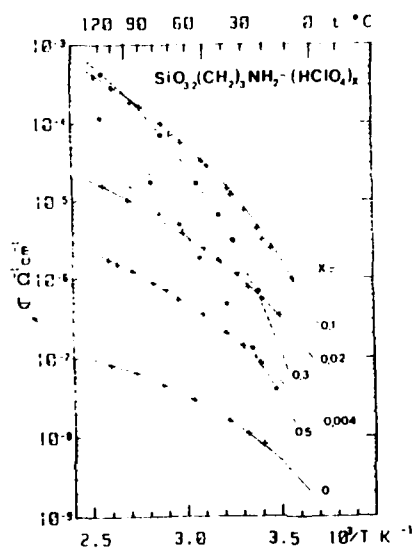


FIGURE 1 gives the variation of conductivity σ with temperature for different concentrations of perchloric acid. The variation of σ with temperature is interpreted by the free volume transport theory.



SELF IONISABLE NETWORKS AS SOLID ELECTROLYTES.

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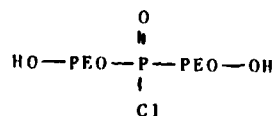
1. Introduction.

Our laboratory has been involved in the research for polymer electrolytes for some years and has concentrated on covalently crosslinked polymers for which it was hoped besides the advantages of solid electrolytes some improved mechanical properties (1,2).

From the point of view of the macrostructure the electrolytes based on organic polymer network can be divided into two classes, i.e. the networks containing the ionisable functions under the form of salts dissolved or dispersed in the material and the networks for which the ionisable functions are covalently linked to the macromolecular chains. This second class is sometimes called self-ionisable polyelectrolytes.

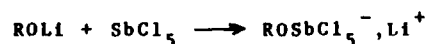
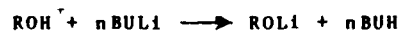
2. Synthesis of self ionisable networks.

The synthesis of self ionisable networks brings new problems because the cations being generally solvated by interactions with the chain segments the material is more or less a solid or a material of high viscosity, being crosslinked or not. There are two ways of obtaining these materials, either the ionisable functions are introduced before crosslinking and this last operation is very difficult due to the high viscosity of the system, or the crosslinking reaction is achieved before the introduction of the proper ionisable function. Thence, this last operation must be done within a solid. This is always difficult even if the solid has a high swelling ability. Limitation of the ionisable functions content to get a better processability is detrimental to the final conductivity of the electrolyte. Up to now the success of the synthesis of a given material is the result of a delicate balance between contradictory technical requirements. To our best knowledge there are only few attempts to produce self ionisable networks (3-6). In our laboratory the most studied system is obtained by reaction of one mole of POCl_3 or PSCl_3 with two moles of PEO glycol:

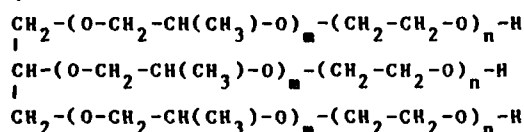


then followed by crosslinking by the usual polyurethane technology after being hydrolysed then neutralised by

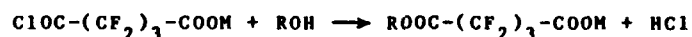
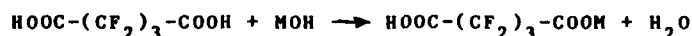
lithium hydroxide. In another example self ionisable networks are synthesised from a polyol on which part of the hydroxylic groups have been transformed into the lithium salt of complex anions, according to (4):



the remaining hydroxylic functions borne by the radical R being used for crosslinking. In this context we have used polyether triol (MW = 2600), corresponding to the structure:



or comblike polymers such as poly(dimethylsiloxane) grafted with polyether. The polyether branches consist of a two blocks copolymer poly(ethylene oxide-b-propylene oxide). The preparation of these materials is difficult, particularly when the grafted siloxane is used. Monosalts of perfluorinated dicarboxylic acids have been also used to functionalize polyether polyols before crosslinking according to the following chemistry:



where M is the lithium metal, and ROH is actually the same polyether triol as the one described above.

Generally, the system to be crosslinked is placed inside a mold consisting in two glass plates separated by a joint of known thickness so as to obtain the materials under the shape of a calibrated membrane. This technology has been used in the case of networks filled by salts as well.

3. Transport properties of self ionisable networks.

3.1. Dynamic mechanical properties

Dynamic mechanical properties have been studied for some self ionisable networks based on the oxy- and thio-phosphorous trichloride chemistry described above (section 2). Measurements have been performed at 11 Hz. The same general behaviour as in the case of polyether networks filled with salts has been observed (3). The problems linked with the synthesis are sometimes reflected in the width of the relaxation spectrum.

It is worth noting that the glass transition temperature is decreasing with increasing molecular weight of the polyol used for the synthesis, i.e. with the decreasing concentration of the ionisable functions.

3.2. Magnetic nuclear relaxation.

Molecular processes characterised by low relaxation frequencies can be examined through the transverse magnetisation relaxation function (3). The movements and the "freezing" of the ions follow closely the extent of segmental motions allowed at the considered temperature, as can be seen for the linewidth of the resonance of the ^{31}P (belonging to the anions linked to the chains), and ^1H (belonging to the chain segments) nuclei. This result is easily accounted for assuming that the movements of chain segments represent the limiting process the fluctuations of the local free volume which is at the origin of the movements of these three nuclei.

This fact strongly supports the interpretations given for the general explanation of the transport properties of the electrolyte networks. But probably the most interesting finding in these last experiments is that the self ionisable networks behave in a similar way as the networks filled with salts.

3.3. Ionic conductivity.

The ionic conductivity of some self ionisable networks based on the phosphorous chemistry described above has been studied by the well-known complex impedance plot method.

The results showed that generally the conductivity is rather poor, being around $10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at 100°C . As already observed for networks filled with salts, a decrease of the glass transition temperature brings about an increase of the conductivity. The networks synthesised with phosphorous thiotrichloride exhibit a higher conductivity than the one of the networks based on phosphorous oxychloride, in spite of a higher glass transition temperature. This result is explained assuming a higher dissociation degree of the ionisable functions. This interpretation was confirmed by the fact that the introduction in the network of a solvent of a high dielectric constant largely improved the conductivity.

The ionic conductivity of membranes based on polyether triol (MW = 2600) bearing one perfluorinated lithium carboxylate function per chain was slightly higher than the one of the poly(siloxane) grafted with polyether (total MW = 9200). This observation is consistent with the previous finding that the conductivity of membranes composed of a polyether network filled with an ionisable salt was strongly dependant on the crosslinking density. The conductivity observed in the case of the self ionisable networks based on the above triol and the lithium alkoxypentafluoroantimonate function was fair, corresponding to one ion per initial

macromolecular chain before crosslinking, better than 10^{-6} Ohm cm^{-1} at 25°C. The better conductivity of this last material is assigned to the better dissociation of the functions.

3.4. Ionic transport numbers .

Only a few studies have been devoted to the evaluation of the cationic and the anionic transport numbers. This study has been done using the well established Tubandt's method (7). Applying this technique to membranes based on various polyethers and of different structures and crosslinked with the usual polyurethane technology some important conclusions have been drawn: most of the electrolyte polyether networks filled with salts have a predominant anionic conductivity, and the use of perchlorates gives a relatively low cationic transport number, even with the lithium cation. These results, rather unexpected, explain the high interest of the self ionisable networks which allow the obtention of materials of a specific conductivity, i.e. totally cationic for instance. Indeed it has been verified that the self ionisable networks based on the phosphorous oxychloride chemistry described above (see section 2) have a cationic transport number equal to unity within the experimental errors (4). Then the free volume conductivity behaviour observed here means that the cations can move only if they have a hole of sufficient size in their vicinity, alike the anions in the networks filled with salts previously studied.

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NMR AND CONDUCTIVITY STUDY OF ANHYDROUS POLYMER PROTONIC CONDUCTORS

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The study of the complexes between poly(ethylene oxide), PEO, and various alkali metals salts has attracted considerable attention during the last decade (1). Recently, this concept has been extended to anhydrous protonic polymer conductors by the synthesis of complexes between PEO and the Phosphoric acid. These compound $\text{PEO}(\text{H}_3\text{PO}_4)_x$, where x is the fraction of acid molecule per monomer unit - exhibit a good ionic conductivity at room temperature ($\sigma \sim 4 \times 10^{-5} (\Omega \text{ cm})^{-1}$) (2).

Extensive NMR, σ , DSC studies have been performed on these systems. The present abstract forms part of a comprehensive NMR study including crystallinity, determination of the stoichiometry of crystalline complexes, measurements of diffusion coefficients of ^1H and ^{31}P by the technique of Pulsed Magnetic Field Gradient, and spin lattice and spin spin relaxation rate as a function of temperature and frequency.

Here we present some results of a NMR study on the compound $\text{P}(\text{EO})(\text{H}_3\text{PO}_4)_x$ $x = 0.42$ including T_1 and $T_{1\rho}$ measurements for ^1H and ^{31}P nuclei and preliminary data on the ^1H diffusion coefficient in deuterated $\text{PEO}(\text{H}_3\text{PO}_4)_{0.66}$, which we compare with conductivity data.

Required amount of polymer and acid were weighted and dissolved in acetonitrile (Merk anhydrous) and THF mixture, under a dry argon atmosphere in a glove box (less than 1 ppm H_2O and O_2) to

the desired phosphor : oxygen in PEO ratio.

The NMR relaxation time measurement were performed in the temperature range 227-353 K at 34 MHz. For T_{1P} measurement the RF rotating field H_1 were equal to 5 and 10 G.

Conductivity measurements were performed using the a.c impedance technique over the temperature range 260-345K. Details of experimental cell and procedure have been published elsewhere .

In order to determine the effects of the motion of the polymer chain on the diffusion coefficient, we have plotted the value of the proton correlation time τ deduced from the T_1 minima (where $\omega\tau = 1$, $2\omega_1\tau = 1$) with the conductivity data (σT vs $1/T$). Resulting graph, in Figure 1; shows that the τ value scale fairly well with the conductivity data, within the limits of experimental error, showing that the diffusion coefficient is governed by the segmental motion of the chains, as previously observed alkali metal P(EO) complexes (3).

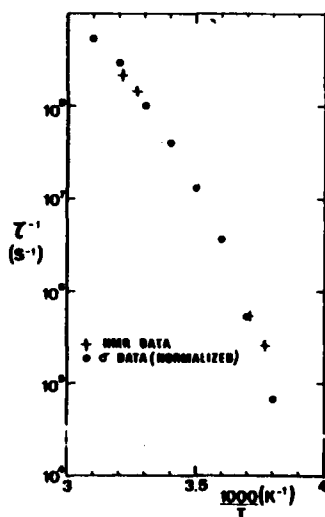


Figure 1 : Temperature dependence of the proton correlation time deduced from NMR data on $PEO(H_3PO_4)_{0.42}$ with the value deduced from conductivity data.

We shall now focus on the ^{31}P NMR data in $P(EO)(H_3PO_4)_{0.42}$ and especially on the case of deuterated acid. The reason is that in this case we suppress two sources of relaxation, the intramolecular H-P interactions, and the polymer-acid H-H interactions, thus making easier the interpretation of the relaxation mechanisms. In Fig.2 is shown the temperature dependence of the spin-lattice relaxation rate of ^{31}P . Several points have to be noticed. The peak in T_{1P}^{-1} observed around 260K has the same amplitude for both deuterated and undeuterated acid (not shown in the figure). Consequently, its origin has to be attributed to a modulation of the interaction between the protons of the chain and the phosphorous.

The frequency dependence of our T_1 and $T_{1\rho}$ data strongly departs from the classical BPP picture which predicts a quadratic dependence on frequency for the relaxation rates.

A convenient way to describe relaxation processes in disordered systems is to use the so-called stretched exponential correlation function (4)

$$f(t) = \exp \left[(-t/\tau)^\beta \right] \quad (1)$$

in such a description, the spin lattice relaxation time in the low temperature region, where $\omega_0 \tau \gg 1$ has the form :

$$T_1 \propto \omega_0^{1+\beta} \tau^\beta \quad (2)$$

We made an estimate of this parameter β from an implicit plot of σT versus the spin-lattice relaxation rate in this temperature range, assuming that σT is proportionnal to $\tau(T)^{-1}$, which leads to a value of $\beta=0.27$ (Fig.3).

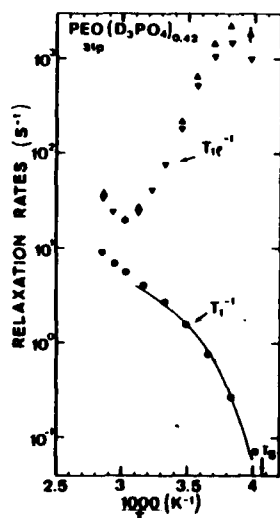


Figure 2 : Temperature dependence of the phosphorus spin lattice relaxation rate at $\omega_0 = 34$ MHz in $\text{PEO}(\text{D}_3\text{PO}_4)_{0.42}$ ($H_1 = 5G$; $H_2 = 10G$).

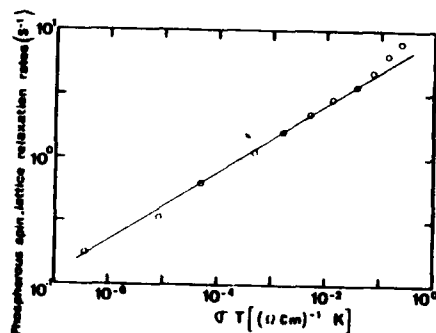


Figure 3 : Logarithmic plot for Phosphorous spin-lattice relaxation rate T_1^{-1} of $\text{PEO}(\text{D}_3\text{PO}_4)_{0.42}$ versus T data.

Using this value, and a correlation time $\tau(T) = \tau_0 \exp(E/k(T-T_0))$, where $E=0.05$ eV and $T_0=224$ K are the value obtained from the conductivity data, we obtain a good fit of our NMR data. From the $T_{1\rho}^{-1}$ maxima condition we obtained $\tau_0 = 1.67 \cdot 10^{-12}$ s. The T_1^{-1} temperature dependence in the temperature range is well reproduced, and we also get the correct frequency dependence between our T_1 and $T_{1\rho}$ data.

Finally, we have determined the diffusion coefficient of the proton ^1H in a deuterated $\text{P}(\text{EO})(\text{H}_3\text{PO}_4)_{0.66}$. Comparison with the conductivity data indicates that only a small fraction of the mobile species participate to the charge transport. Further measurements are currently in progress.

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POLYMER ELECTROLYTE COMPLEXES OF LITHIUM PERCHLORATE
AND POLY{(METHOXPOLYETHYLENE GLYCOL)METHYLSILOXANE}S

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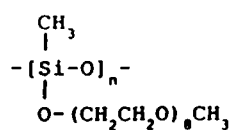
INTRODUCTION

Ionic conduction in solvent-free polymer electrolytes primarily occurs in the amorphous domains via a free volume mechanism (1). The need for good mobility of polymer chain segments has led to the synthesis of novel polymers with pendant oligo-oxyethylene side chains and a polyphosphazene (2), poly(methacrylate) (3,4), polybutadiene (5) or polysiloxane (6,7) backbone. This report describes the synthesis of some comb-type poly{(methoxypolyethylene glycol)methylsiloxane}s and the conductivity of their complexes with lithium perchlorate.

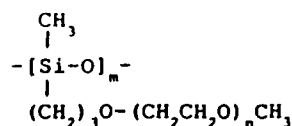
EXPERIMENTAL

Poly{[ω -methoxyhepta(oxyethylene)ethoxy]methylsiloxane}, abbreviated as PMMS-8, was prepared by reacting methoxypolyethylene glycol of MW 350 with poly(hydrogenmethylsiloxane) (MW 2650) in THF at 60°C with zinc octanoate as catalyst. The NMR spectrum indicates an average of eight ethylene oxide units per side chain rather than seven as previously reported (6).

Poly{[ω -methoxyoligo(oxyethylene)propyl]methylsiloxane}s were prepared from poly(hydrogenmethylsiloxane) and the allyl ether of methoxy polyethylene glycols of MW 350 and 550, respectively, in THF at 50°C using platinum-divinyltetramethyldisiloxane as catalyst. The allyl ether was made from allylchloride and the methoxypolyethylene glycol in THF with NaH at 25°C. The two polymers, abbreviated as PAGES-8 and PAGES-12 have an average of 8 and 12 ethylene oxide units in the side chain. The structures of PMMS-8 and PAGES-n are shown below.



PMMS-8



PAGS-n where n = 8 or 12

Complexes of the three polymers with LiClO_4 were made by evaporation of solvent from a polymer-salt solution in THF, followed by careful drying under vacuum. Cross-linked complexes of PMMS-8 were prepared by adding 1% by weight of benzoyl peroxide to the complex and heating the sample for 24 hrs. at 100°C (6). Polymer blends of PEO ($M_n = 4 \times 10^6$) and PMMS-8 were obtained by solvent evaporation of a methanolic solution of PEO, PMMS-8 and LiClO_4 , followed by vacuum drying at $50-60^\circ\text{C}$ for several days.

The polymers were characterized by 100 MHz ^1H NMR, ^{29}Si NMR, IR and FTIR, and GPC with THF as eluant. Details of DSC and conductivity measurements (AC) have been reported elsewhere (3,6).

RESULTS AND DISCUSSION

^1H NMR and IR spectra indicate complete conversion of Si-H groups for PMMS-8 and PAGS-8. For PAGS-12 the conversion is better than 90% complete. ^{29}Si NMR and GPC data do not show the presence of low molecular weight cyclics in PAGS-8 and PAGS-12. However, in PMMS-8 the weight % of low molecular weight cyclics may be as high as 30%.

Conductivity measurements on the LiClO_4 complexes as a function of temperature yield linear plots when using the Vogel-Tamman-Fulcher relationship. Maxima in the conductivities are found at ethylene oxide unit to Li^+ ratios of about 25. Table I lists the conductivities σ (in $\text{ohm}^{-1}\text{cm}^{-1}$) at 25°C and 70°C for LiClO_4 complexes with the three polymers and the cross-linked PMMS-8 at the ratio $\text{EO/Li} = 25$. The higher weight fraction of ethylene oxide units in PMMS-8 relative to PAGS-8 (with its rather large hydrophobic backbone region) makes the former polymer a better conducting medium. This is also the reason for the higher σ of PAGS-12 relative to PAGS-8. The advantage of the PAGS polymers vis a vis the PMMS-polymers are the higher stability of the Si-C linkage as compared to Si-O-C.

The dimensional stability of the polymer electrolyte complexes (all viscous oils) can be improved by cross-linking or blending with PEO. Cross-linking lowers the conductance as it impedes segmental chain motion (Table I). Addition of PEO to a LiClO_4 /PMMS-8 mixture changes the complex into a blend from which tough, flexible films can be cast. Figure 1 depicts the conductance behavior of these polymer electrolyte films as a function of the ratio Li^+/EO . The room temperature conductance of these films at EO/Li ratios of 25 are considerably above $10^{-5} \Omega^{-1} \text{cm}^{-1}$, and far exceed those of $\text{PEO}/\text{LiClO}_4$ complexes. The PMMS-8 acts as a non-migratory plasticizer for PEO with good conducting amorphous domains while PEO imparts dimensional stability to the film.

The financial support of this work by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

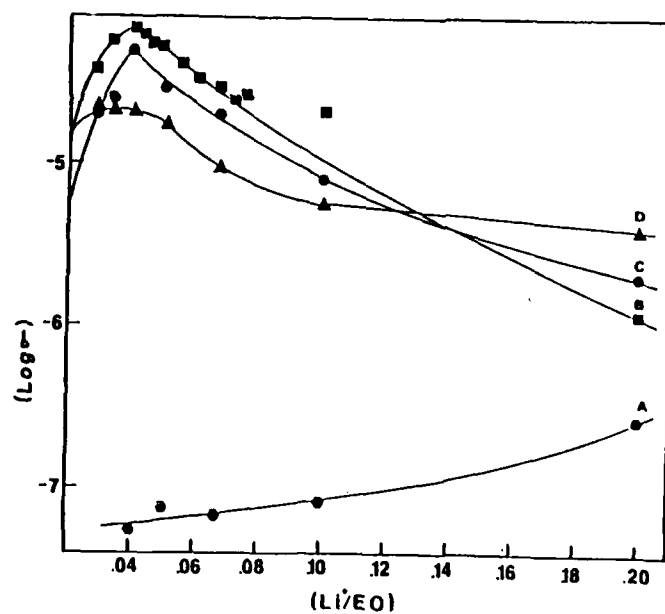
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Table I. Conductivities of Polymer-LiClO₄ Complexes

Polymer	$\sigma \times 10^5, \text{ohm}^{-1}\text{cm}^{-1}$	
	25°C	70°C
PMMS-8	7	25
PMMS-8 (cross-linked)	2	13
PAGS-8	3	
PAGS-12	7.6	46

Figure 1. Plot of log conductivity versus the ratio of Li⁺ to ethylene oxide units for mixtures of LiClO₄ and PEO (A); PMMS-8 (B); 70/30 blend of PMMS-8/PEO (C); 50/50 blend of PMMS-8/PEO (D)



**SOLID POLYMERIC ELECTROLYTES FORMED BY
POLY(ETHYLENE OXIDE) AND NICKEL BROMIDE**

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I. Introduction: Recently, several studies have reported that PEO dissolves a number of salts of divalent cations to form polymeric electrolytes with appreciable ionic conductivities (1-5). This work has expanded upon earlier reports of James et al. (6,7); it demonstrates that the family of PEO-based quasi-solid electrolytes is actually quite large and that PEO and similar polymers behave more like unusual non-aqueous solvents than crystalline solid electrolytes.

We have recently been studying PEO electrolytes formed with salts of divalent cations and monovalent anions. These include compositions with salts of Mg(II) (4), Zn(II) (8), and Pb(II) (5), and others. This paper describes some of our investigations of PEO containing NiBr₂. We were quite surprised to find that the Ni²⁺ transport number in these materials can be increased by a process involving the slow hydration and dehydration of the electrolytes after they have been prepared.

II. Film Preparation: (PEO)_xNiBr₂ electrolytes were prepared by solution casting using a two-solvent technique. NiBr₂ was dissolved in anhydrous ethanol and PEO (Polysciences, MW=5x10⁶) in acetonitrile. Solutions of NiBr₂ and PEO were then mixed and electrolyte films cast on a Teflon™ plate. Solvent was first allowed to evaporate at room temperature in a dessicator over molecular sieves. Electrolyte films were then heated to 140°C in vacuum to remove residual solvent.

In the remainder of this abstract, the following terms will be used to denote the origins of various samples: 'as cast' is a sample that was cast and then de-solvated at room temperature in a dessicator; 'as cast and dried' means the sample was cast and residual solvent removed by heating to 140°C; 'modified' means the sample was heated to 140°C, cooled to room temperature and hydrated in moist gas, and then dehydrated by heating to 140°C in a stream of dry argon or nitrogen.

III. Results and Discussion

A. Thermogravimetric Analysis: During the initial heating of a freshly-prepared film of (PEO)₈NiBr₂, there was a gradual loss in weight between room temperature and 80°C but no further weight loss before heating was discontinued at 200°C. When the

sample was then cooled in dry nitrogen and re-heated, the low-temperature weight loss did not re-appear, and the sample weight was stable until decomposition commenced around 330°C.

TGA also showed that sample films rapidly hydrate when exposed to water vapor at room temperature. For example, when a sample of (PEO)₈NiBr₂ was allowed to hydrate in moist air for 24 hours at room temperature, it absorbed about 30 molecules of water per (PEO)₈NiBr₂ unit. When the sample was then held in flowing dry nitrogen at room temperature for 24 hours, it lost all but 6 molecules of water per (PEO)₈NiBr₂. The remainder of the water could be removed by heating to 140°C.

These results indicate that there is both weakly and strongly-bound water in hydrated samples of (PEO)₈NiBr₂. The strongly-bound water, which can only be removed upon heating to 140°C, corresponds to water in the hexaquo complex (PEO)₈NiBr₂·6H₂O. The existence of this complex was confirmed by optical spectroscopy measurements.

B. Conductivity Measurements: Polymer film conductivities were measured by complex impedance/admittance analysis from 10² to 10⁶ Hz with both blocking (Pt) and non-blocking (Ni) electrodes. The values determined for bulk conductivity were the same for both types of electrode, but the use of Ni electrodes made it possible to estimate the Ni²⁺ transport number. Before analysis, all samples were dried in the conductivity cell under vacuum, first overnight at room temperature and then at 140°C for 2-3 hours. Measurements were then carried out in a stream of purified argon.

The conductivity of a sample of (PEO)₈NiBr₂ during heating and cooling is shown in Fig. 1. The conductivity knee around 60°C is a feature generally expected in samples of these materials from the melting of uncomplexed PEO. The conductivity undergoes an unexpected dip around 130°C and then gradually increases at higher temperatures.

What is quite surprising is the effect that hydration and dehydration have on the Ni²⁺ transport number in (PEO)₈NiBr₂. As Fig. 1 shows, above 60° the conductivity of the modified electrolyte is much greater than that of the as cast/dried electrolyte. Modified samples are not only more conductive, they also have much higher transport numbers for Ni²⁺.

The transport numbers of Ni²⁺ in normal and modified samples were estimated using complex ac impedance analysis and dc polarization with non-blocking Ni electrodes. The result of both sets of experiments show that the transport number of Ni(II) normal sample is quite low, even at 140°C, whereas the modified sample shows appreciable Ni²⁺ transport. Fig. 2 plots log $t_{Ni(II)}$ vs. temperature. As the data show, the normal film is virtually a pure anion conductor, while the modified sample has considerable Ni²⁺ mobility. This effect was repeated on sample after sample. No sample was ever measured that did not show the effect.

IV Conclusions

Electrolytes formed by dissolving NiBr_2 in PEO are unusual in that the transport number of Ni^{2+} can be apparently be enhanced by controlled hydration and dehydration. The same process also results in a dramatic increase in conductivity above 60°C . Preliminary measurements of the UV-visible spectroscopy of $(\text{PEO})_8\text{NiBr}_2$ show that during hydration water first associates with Ni(II) to form the hexaquo complex. TGA data indicate that essentially all Ni(II) in the electrolyte forms this complex. It may be that the complex formation frees the Ni(II) from a strong interaction with the ether groups in the PEO chains set up when the electrolyte is formed. The structure of the electrolyte must obviously be very different after dehydration than before, since there is such a large increase in conductivity. The high conductivity form may be metastable, but no sign that the complex reverts to the low conductivity form has been observed.

Figure 1. Conductivity of $(\text{PEO})_8\text{NiBr}_2$; normal sample (o); modified sample (x).

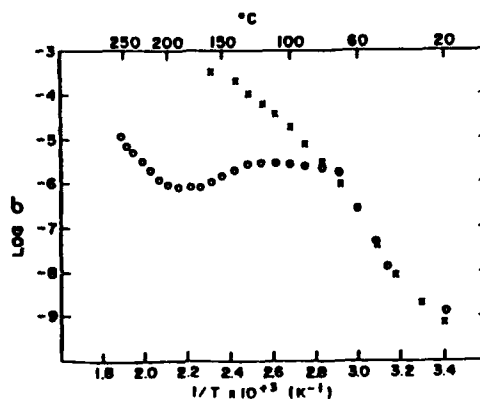
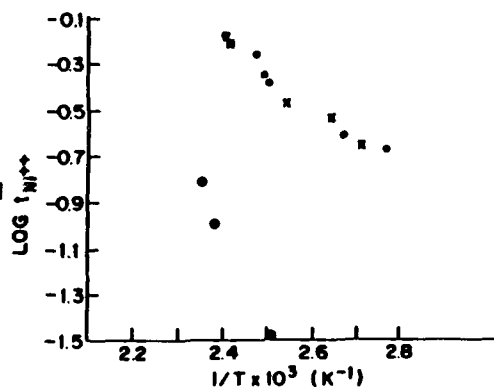


Figure 2. Plots of $\log t_{\text{Ni}}$ vs. temperature for normal sample (dotted circles); for modified (solid circles); and for modified repeat after 7 days (x).



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Electroactive Polymer Blends

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INTRODUCTION

The rapid development of the two new classes of electrically active polymer materials, electronically conducting and electroactive polymers and ion conducting polymers respectively, offers new possibilities for application of both materials, especially in combination with each other. While some of these combinations have been attempted earlier, they all met serious problems due to poor interpenetration of the two polymers. The recent availability of solubilized electroactive and conductive polymers have greatly advanced the possibilities of reducing the interpenetration problem. We present some experimental studies using the combination of solubilized electroactive polypyrrole with polyethylene oxide in a electroactive polymer blend electrode for solid state polymer batteries. We also discuss the general possibilities of using polymer blends for solid state electrochemical polymeric devices, and avenues for materials development for such devices.

SOLID STATE POLYMER BATTERIES

Electroactive polymers can be dispersed in ion conductive polymers by mixing suspensions or solutions of both types of polymers and solution cast these mixed polymers. To reach an high degree of dispersion the polymers should exist as very fine particles or as polymer molecules. This is no problem for the polymer electrolytes but has been quite a problem for electroactive polymers. Recently, techniques for making suspensions of polypyrrole in water, by using a polymer stabilization technique, have become available(1). We have used this technique to make polymers blends with polyethylene oxide(2,3) for preparing composite

polymer electrodes for polypyrrole/Li batteries. These polymer blends strongly enhance the coulombic capacity of the electrode, as more of the electroactive material is in close contact with the electrolyte. The shorter paths of diffusion of intercalating ions within the electroactive polymer, due to the small dimensions of the polymer particles, also enhances the rate of utilization. Our studies show the main and great problem to be the extremely rapid rate of selfdischarge in the battery. We present a theoretical analysis of the energy density of solid state polymer batteries utilizing polymer electrolytes in combination with Li and/or electroactive polymer electrodes.

PROSPECTS FOR DEVICE DEVELOPMENT

The use of polymer blends in electrochemical devices has been demonstrated in secondary batteries but is not limited to these. Electrochromic devices incorporating such polymer blends could be constructed. Photoelectrochromic devices incorporating polymer electrolytes should be possible(4). There exists considerable scope for synthesis of electroactive polymers that have the "right" spectral features for application in electrochromic windows. For instance the conductive polymer poly(isothianaphtene) has been shown to have a very low bandgap and is transparent in its oxidized state and black in the neutral state. (5)

AVENUES FOR MATERIALS DEVELOPMENT

The use of electroactive polymer blends reduces the problems encountered during ion transfer at the interface between electroactive polymers and ion conductive polymers. It does this mainly by enormously enhancing the contact area between the phases, in the case of the microheterogeneous blends. This might be a rather trivial way of solving a problem that is more fundamental. One of the advantages

that we expect to exploit in this geometry is the short diffusion paths that are encountered on charge and discharge of the electroactive particles. On the other hand, if we could enhance the diffusion properties of ions in the electroactive polymer, we could maybe combine the electroactive and ion diffusion properties in one and the same polymer molecule. The race for higher conductivity in polymer electrolytes will require an qualitative understanding of the role of polymer dynamics in the transport process. If these mechanisms could be incorporated in electroactive polymers we might find a completely new class of molecular composites incorporating both electroactivity and facile ion diffusion. It appears quite probable that these will be conflicting goals, but it may be that the optimum is not that found in presently available materials.

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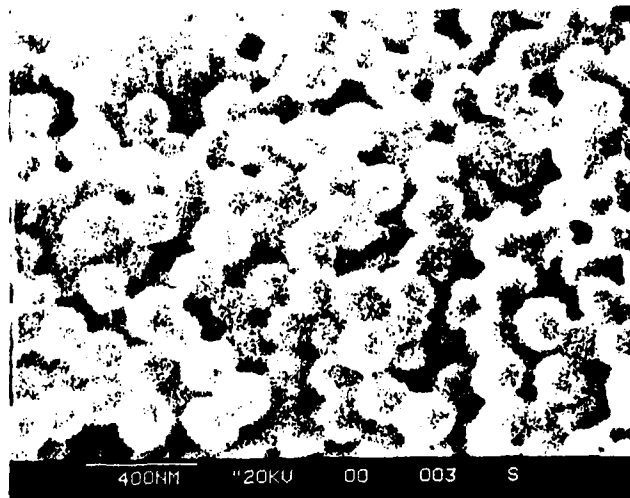


Fig.1 SEM picture of an electroactive polymer blend material(2). The material was prepared by mixing water solutions of solubilized polypyrrole and polyethylene oxide. The mixture contains 30 weight percent PEO and the electronic conductivity is around 0.5 S/cm. The small spherical particles of some hundreds of nm dimension consists of polypyrrole.

Conductivity of polymer electrolytes of lithium salt with acrylate polymer containing tris(methoxy(polyoxyethylene)ethoxy)siloxy alkyl groups.

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Introduction

Recent works for solid polymer electrolytes have focused on lithium salt complexes of polymers such as poly(ethyleneoxide) (1), poly(propyleneoxide) (2), polymethacrylate containing -methoxy-polyoxyethylene chain groups (3), polyphosphazene (4) and polymethylsiloxane (5). The requisites for the ECD polymer electrolytes are transparency and high ion conductivity. In this paper we describe a new polymer electrolyte of lithium salt with acrylate polymer containing tris(methoxy(polyoxyethylene)ethoxy)siloxy alkyl group. The ion conductivity of this polymer electrolyte was $1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 25°C , and the transparency was 96% at 400-800nm.

Experimental

Acrylic macromers containing tris(methoxy(polyoxyethylene)ethoxy)siloxy alkyl groups were prepared according to scheme 1. To a toluene solution (80ml) containing 0.4 mol of SiCl_4 , 0.1 mol of acrylic monomer was added dropwise at 5°C . The mixture was stirred for further 3h and the excess of SiCl_4 was removed by vacuum distillation. To this mixture, 200ml of toluene solution containing 0.4 mol of pyridine and 0.3 mol of methoxy poly(ethylene glycol) was added dropwise at 20°C and then the mixture was stirred for further 4h. The mixture was filtered to remove the pyridine·HCl salt and toluene was removed from the mixture by vacuum evaporation. The crude product was washed with n-hexane and diethyl ether to yield the macromer.

Polymer electrolyte films of lithium salt with acrylate polymer were prepared by a casting polymerization method. Macromer, comonomer as a crosslinking reagent, benzoylperoxide (0.5wt%/monomer) and LiX were dissolved in methanol and the

mixture was casted on a glass plate and dried at 60°C for 10h under 1 mmHg.

The glass temperatures of films were measured using a Perkin Elmer 990 DSC meter and the ion conductivities were obtained with a Yokokawa-Hewlett-Packard 4274A/4275A multi-frequency LCR meter.

Result and discussion

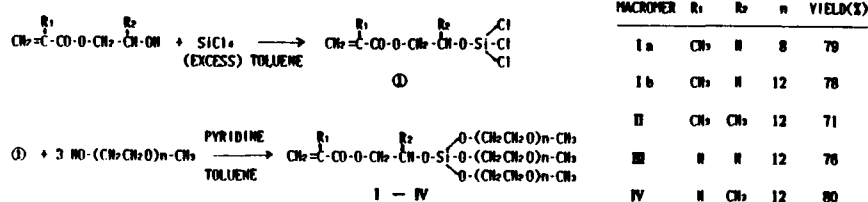
The components, compositions, glass temperatures and ion conductivities of the polymer electrolyte films in this work are summarized in table 1. Figure 1 shows temperature dependence of ionic conductivities for the typical polymer electrolyte films. Figure 2 shows the effects of the EO equivalent in monomers on the ion conductivity.

The glass temperatures of the polymer electrolyte films from macromer I - IV were lower than those of the polymer electrolyte films from methacrylic acid polyethyleneoxide (MPEO) and maleic acid di-polyethyleneoxide macromer (MEPEO) and as a result glass temperatures of polymer electrolyte films from I - IV were higher than those of films from MPEO and MAPEO even at the same EO equivalent.

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SCHEME 1 PREPARATION OF MACROMER
ACRYLATE DERIVATIVES WITH TRIS [METHOXY(POLYOXYETHYLENE)ETHOXY] SILOXY ALKYL GROUPS



MACROMER	R ₁	R ₂	n	YIELD(%)
Ia	CH ₃	H	8	79
Ib	CH ₃	H	12	78
II	CH ₃	CH ₃	12	71
III	H	H	12	76
IV	H	CH ₃	12	80

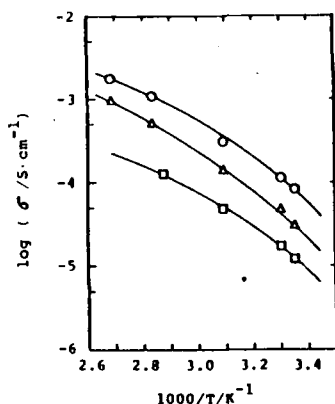


Fig. 1. Temperature dependence of ionic conductivity of films: (○), film No. 9; (Δ), film No. 4; (□), film No. 2 in table 1.

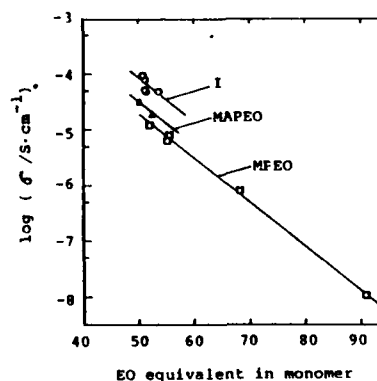


Fig. 2. Relation between logarithm of ionic conductivity and EO equivalent in monomer. Macromer in films: (○), macromer I; (Δ), macromer MAPEO; (□), macromer MPEO. [EO unit]/[LiX] in film is 18. The ratio of macromer/[comonomer (PEGDM)] in film is 75/25.

TABLE I IONIC CONDUCTIVITY OF FILMS

FILM No.	MACROMER STRUCTURE	n	SALT	COMPOSITION OF FILMS (wt %)		ED UNIT ED. IN MONOMER	ED UNIT ² (CIX)	T _g (°C)	CONDUCTIVITY (at 25°C) 10 ⁵ x σ (S/cm)
1	CH ₂ =C(CH ₃)CO-O-(EO)n-CH ₃ (MPEO)	8	LiClO ₄	67.7	22.8	9.7	55.1	-49	0.63
2	CH ₂ =C(CH ₃)CO-O-(EO)n-CH ₃	12	LiClO ₄	67.3	22.4	10.2	51.9	-52	1.2
3	CH ₂ =C(CH ₃)CO-O-(EO)n-CH ₃	8	LiClO ₄	67.4	22.5	10.1	52.4	-48	1.9
4	CH ₂ =C(CH ₃)CO-O-(EO)n-CH ₃ (MPEO)	12	LiClO ₄	67.1	22.4	10.5	50.2	-52	3.1
5	CH ₂ =C(CH ₃)CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃	8	LiClO ₄	67.5	22.5	10.0	53.5	-66	4.7
6	CH ₂ =C(CH ₃)CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃	8	LiBF ₄	68.3	22.8	8.9	53.5	-68	3.2
7	-Si(CH ₃) ₂ -O-(EO)n-CH ₃	8	LiCF ₃ SO ₃	64.5	21.5	13.9	53.5	-68	3.9
8	(I a)	8	LiPF ₆	64.8	21.6	13.6	53.5	-66	3.4
9	CH ₂ =C(CH ₃)CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃	12	LiClO ₄	67.2	22.4	10.4	50.9	-63	8.2
10	CH ₂ =C(CH ₃)CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃	12	LiBF ₄	68.0	22.7	9.3	50.9	-65	5.1
11	-Si(CH ₃) ₂ -O-(EO)n-CH ₃	12	LiCF ₃ SO ₃	64.1	21.4	14.5	50.9	-67	3.9
12	(I b)	12	LiPF ₆	64.3	21.4	14.2	50.9	-62	5.0
13	CH ₂ =C(CH ₃)CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃ (II)	12	LiClO ₄	67.2	22.4	10.4	51.1	-60	4.8
14	CH ₂ =CH-CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃ (III)	12	LiClO ₄	67.1	22.4	10.5	50.6	-61	9.8
15	CH ₂ =CH-CO-O-CH ₂ -CH ₂ -O-(EO)n-CH ₃ (IV)	12	LiClO ₄	67.2	22.4	10.4	50.9	-60	5.0

a) COMONOMER: PEGDM (POLYETHYLENE GLYCOL DIMETHACRYLATE n=23)
(MACROMER/COMONOMER=1/25)

THE CONDUCTIVITY BEHAVIOUR OF GAMMA IRRADIATED PEO-LiX
ELECTROLYTES

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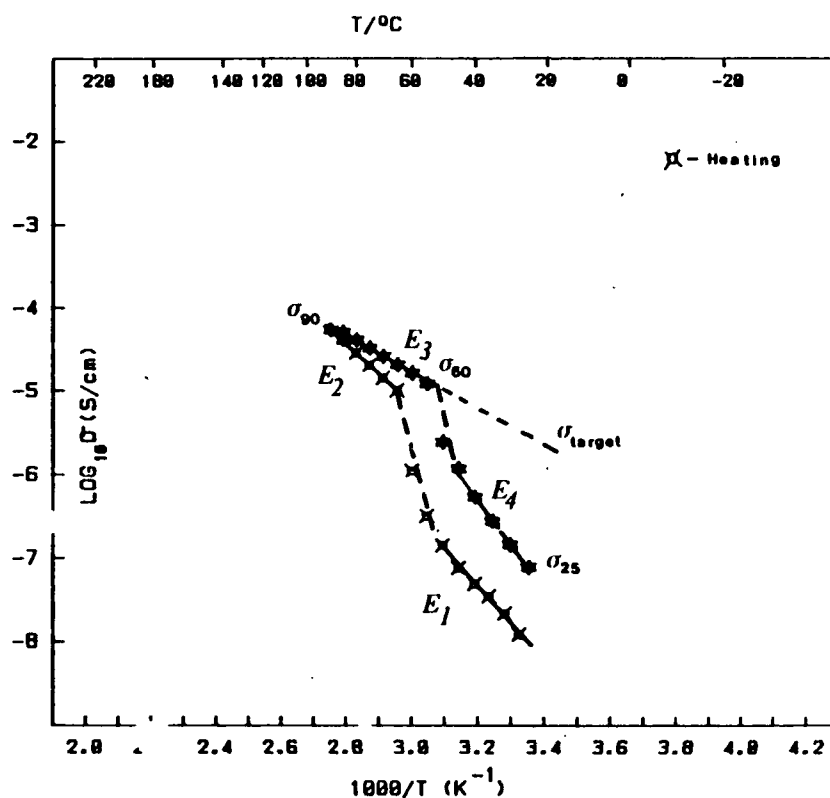
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Polymer electrolytes of the type PEO-LiX have been the subject of a worldwide research effort. This research is partly stimulated by the potential use of the electrolytes in solid-state lithium battery systems. Batteries of this type have been fabricated and studied at the Harwell Laboratory [1], utilising a V_6O_{13} composite cathode and a $PEO_9:LiCF_3SO_3$ electrolyte.

The figure shows the variation in ionic conductivity with temperature for a typical solvent-cast film of $PEO_9:LiCF_3SO_3$. The conductivity/temperature behaviour can be represented by four linear regions with associated activation energies E_1 - E_4 , separated by regions associated with polymer phase change (dotted lines). Three values of conductivity obtained on the cooling cycle (σ_{ss} , σ_{ss} and σ_{23}), combined with the four activation energies, provide a complete description of the conductivity/temperature dependence of the electrolyte.

The transition from E_1 to E_2 is associated with the melting of the PEO phase and, recrystallisation on cooling gives rise to the transition from E_2 to E_4 . This recrystallisation event results in a σ_{23} value which is too low for high current density, room temperature applications. Preventing recrystallisation would result in a higher σ_{23} value (σ_{target}).

One of several methods available to retard crystallisation in polymeric systems is the introduction of cross-links into the amorphous form. Charlesby [2] has shown that gamma irradiation can be used for this purpose, and Vincent et al. [3] have recently applied this method to PEO-LiX electrolytes, using gamma



irradiation to suppress crystallisation in a $\text{PEO}_8:\text{LiClO}_4$ electrolyte.

A study of gamma irradiation at an elevated temperature on the electrolyte $\text{PEO}_8:\text{LiCF}_3\text{SO}_3$ has been undertaken here. Differential Scanning Calorimetry and ionic conductivity results will be presented, and the effects of gamma irradiation on the parameters E_1 - E_4 and σ_{90} , σ_{60} , σ_{25} reported. These results will also be compared to those for a second electrolyte $\text{PEO}_{20}:\text{LiClO}_4$. This, in contrast to the $\text{PEO}_8:\text{LiCF}_3\text{SO}_3$ electrolyte, is totally amorphous at the irradiation temperature.

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HIGH FREQUENCY IMPEDANCE OF AN AMORPHOUS POLY(ETHYLENE OXIDE)

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INTRODUCTION

This work addresses the problem of obtaining accurate impedance data on highly conducting electrolytes at high frequencies. Such data are important for at least the following reasons:

- 1) The dielectric relaxation parameters can provide a conductivity value unaffected by uncertainties in cell geometry, e.g. sample thickness, wetted electrode area.
- 2) Anomalous frequency dependence effects can indicate sample inhomogeneity and fundamental conductivity parameters.

The measurement of the dielectric relaxation in highly conducting samples requires a high frequency range. This may cause problems due to interference from the capacitance and inductance of the cell and connecting leads. For example, above 1MHz the capacitance of a lead can easily mask that of the sample if the area/thickness ratio is less than, say, 100cm, so that the observed impedance plane semicircle is quite artificial. The inductance is also a major problem with samples of resistance less than, say 100 Ohms. The following theory shows how appropriate corrections to the data can be made in the example of a highly conducting amorphous polyether.

EXPERIMENTAL

Two types of sample holder were used; these are shown in Fig.1. Both are designed to hold a small sample in a fixed geometry without excessive creep during measurement. In one, the sample length and area are large enough to be precisely measured, although uncertainty in the real contact area of a non-wetted electrode may be a source of error. In the other, the length is too short for accurate measurement and may even vary across the sample area, although the design minimizes such errors.

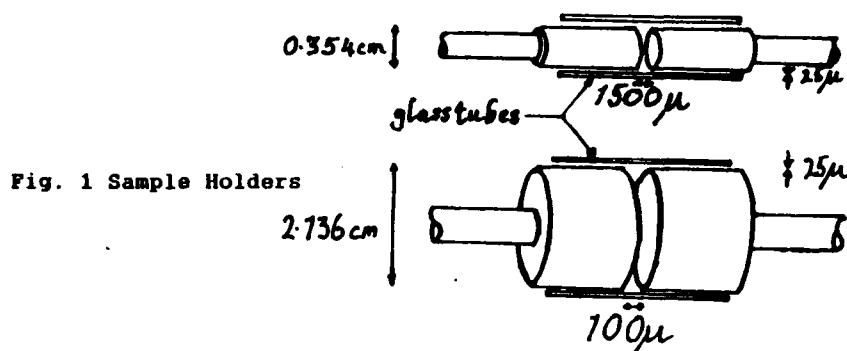


Fig. 1 Sample Holders

The polished electrodes were housed within an argon-filled, temperature-controlled, furnace and connected along short leads through an external co-axial cable to a Hewlett-Packard 4192A impedance analyser.

Impedance and admittance spectra were taken in the range 13 MHz to 5 Hz. Impedance and admittance spectra were also taken of the empty cells in short and open circuit configurations in order to determine the impedance characteristics of the cell, leads and cable combination.

The sample was an oxyethylene-oxyethylene copolymer doped with one LiClO₄ per 24 ether oxygens.

THEORY

The effect of a co-axial cable on the measured impedance value can be shown to be:

$$Z_{app} = Z \left(1 + \frac{Z_s}{Z} \right) \quad \text{where } Z = \text{sample impedance}$$

$$\frac{1}{Y_{app}} = \frac{1}{Y} \left(1 + \frac{Y_o}{Y} \right) \quad Y = \text{sample admittance}$$

$$Z_s = \text{short impedance}$$

$$Y_o = \text{open admittance}$$

$$Z_{app} = \text{measured value}$$

Apparent values may therefore be corrected:

$$Z = \frac{Z_{app} Z_s}{Z_{app} (Y_{app} - Y_o)}$$

RESULTS AND DISCUSSION

Table 1 shows a comparison of the relevant sample, short and open circuit impedance data. It may be seen that in the thick cell no correction due to Z_s is necessary, while Y_o completely swamps any admittance due to the sample; attempts at correction are probably futile. However, in the thin cell, both corrections are useful in the 1MHz region.

Frequency	Z''_s	R_{thick}	R_{thin}	Y_o''	G_{thick}	G_{thin}
Hz	ohm	ohm	ohm	mS	mS	mS
10M	40			4.6		
1M	4	30K	200	.46	.03	5
100K	.4			.046		

Table 1. Typical sample data compared with cell and lead characteristics.

Fig.2 shows the completely artificial dielectric semicircle given by the thick cell. Fig.3 shows a real but distorted semicircle given by the thin cell, and Fig. 4 the corrected version.

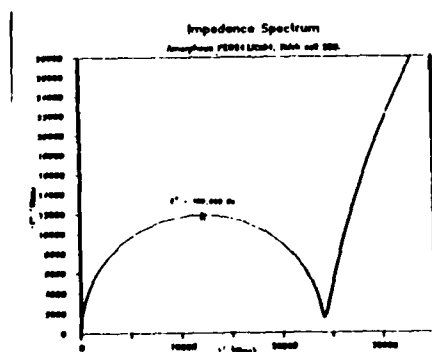


FIG. 2

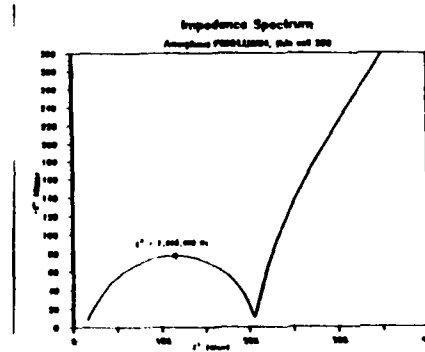


FIG. 3

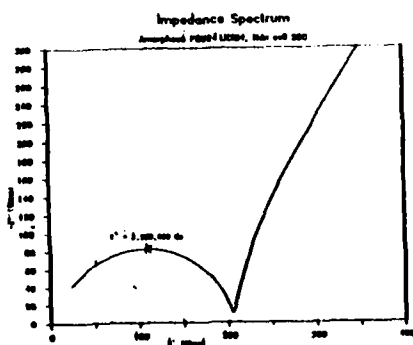


FIG. 4

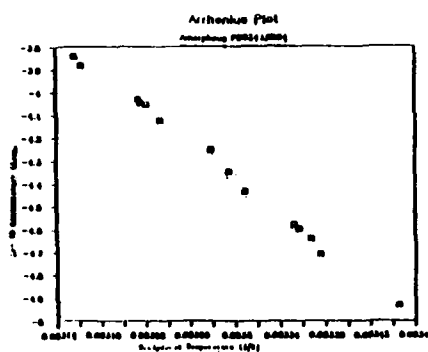


FIG. 5

We conclude that the thick cell gives the most accurate conductivity values, but no information regarding dielectric relaxation. The thin cell showed a semicircle with no detectable depression. Therefore, although no interesting dielectric anomalies were found, we can calculate a dielectric constant. This can be used subsequently to calculate conductivity from high frequency data without a knowledge of the sample dimensions.

An Arrhenius plot for the polymer measured using the thick cell is shown in Fig.5. Extraction of the dielectric semicircle, even from the thin cell becomes increasingly difficult at higher temperatures, and the temperature dependence of the dielectric constant is currently being evaluated.

ACKNOWLEDGEMENTS

The authors wish to thank Dr Colin Booth of Manchester University for providing the (undoped) sample, and Chloride Technical Ltd for financial support.

**SIMULTANEOUS DIFFERENTIAL SCANNING CALORIMETRY/
DIELECTRIC THERMAL ANALYSIS OF POLYMER ELECTROLYTES**

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INTRODUCTION

Two techniques used to characterize polymer electrolytes are differential scanning calorimetry (DSC)(1) and dielectric thermal analysis (DETA)(2). In DSC, heat flow, to and from a sample, is measured as a function of temperature with heating rate as parameter. From these measurements the sample can be characterized in terms of phase behavior, i.e. first or second order transitions, and chemical stability, e.g. dehydration or chemical decomposition. This is a powerful technique which can be used quantitatively both to calculate sample composition and to study the kinetics of physical and chemical transformations. DETA is a more substance-specific technique in which both the real and imaginary parts of the dielectric constant can be obtained as a function of temperature with frequency as parameter. This technique is most sensitive to polymers containing dipoles either in the polymer chain itself or as additives to the system e.g. absorbed water. The frequency dependence of the dielectric constant allows identification of specific types of dipolar motion and characterization of activated processes. When measured isothermally on polymer electrolytes, this technique is known as complex plane analysis (3) and is the standard method used to determine ionic conduction as a function of temperature.

The apparatus and operating conditions used for these two techniques are quite dissimilar and it can be difficult to correlate both sets of data on the same nominal sample, especially when one wishes to study a specific effect e.g. exposure to water vapor, or to undertake precise annealing studies. In order to facilitate analysis of polymer electrolyte samples by these techniques, we have constructed a combined cell in which both measurements can be determined simultaneously, thus allowing precise correlation with temperatures, pretreatment and environmental conditions.

EXPERIMENTAL

A DuPont DSC cell was modified to allow incorporation of a capacitance cell, shown schematically in Figure 1. The sample is kept in good contact with the heat sensor and is thermally isolated from the cell using a spring loaded glass needle above and is electrically insulated with a 2 mil thick Kapton ® film below. Sputtered

gold contacts were applied to polymer films, typically 5x5x0.1mm. Thin copper platens on either side of the film ensured uniform pressure and were connected to isolated binding posts by 3 mil constantan wires. The maximum cell temperature achievable was 170°C and was limited only by use of soft soldered contacts. The dielectric properties of the sample were measured initially with a Hewlett-Packard 4800A Vector Impedance Meter on which both $|Z|$ and phase angle, θ , could be observed on panel meters whose analog outputs were, in turn, fed into a Dynamic Solutions Appligrat data acquisition system. In this way three signals were obtained simultaneously: heat flow (ΔQ), $|Z|^{-1}$, and θ at a single frequency as a function of temperature. In addition, ΔQ and either $|Z|^{-1}$ or θ could be plotted simultaneously during a run on the DuPont 990 XYY recorder using the external input jack. With this system samples could be studied in the temperature range 150K to 450K at heating rates of 2-50 K/min.

It was subsequently possible to study the frequency dependence during a run by using a Solartron 1250 frequency response analyzer programmed with a 9000 series H-P computer so that measurements could be made over the range 6.5 Hz to 65 KHz at 21 different frequencies, once every 10 seconds. The wealth of data obtained in this mode makes it one of the most powerful techniques available for studying polymer electrolytes.

RESULTS

Examples of both techniques are given. Data obtained using the single frequency continuous scan method are shown in Figure 2 for a sample of polyethylene oxide loaded with ZnI_2 of composition $ZnI_2(PEO)_{16}$ at a heating rate of 10°C/min. and frequency of 20 KHz. Effects of glass transition and melting of the pure PEO phase are shown. Figure 3 illustrates the type of information that can be obtained using the multiplexed frequency technique on a sample of $CoBr_2(PEO)_8$ at a heating rate of 10°/min. Figure 3 a) shows the DSC scan and b) and c) show Bode plots before and after the pure PEO phase melts. Dielectric data sets were obtained at 5°C intervals with a temperature spread of only 1.5°C. Continuous scans at fixed frequency similar to those in Figure 2 can be generated for all frequencies measured. Admittance and impedance plots at each temperature allow determination of the bulk resistance and hence ionic conductivity as a function of temperature.

CONCLUSIONS

This powerful simultaneous technique appears suited both for rapid survey and detailed study of the effects of pretreatment and environment on polymer electrolytes.

ACKNOWLEDGMENT. ARM acknowledges support from the National Science Foundation Materials Research Program through grant No. DMR-8519059.

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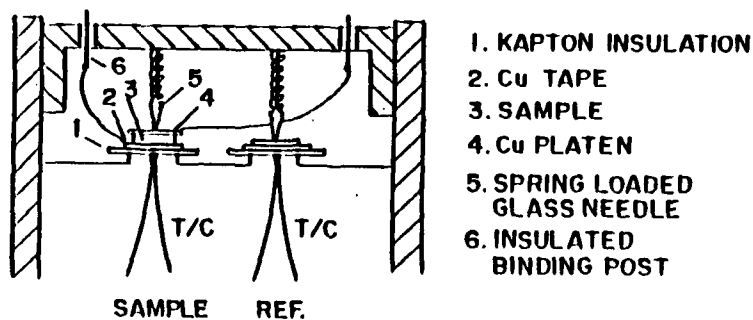


Figure 1. Schematic view of DSC cell modified to include a capacitance cell.

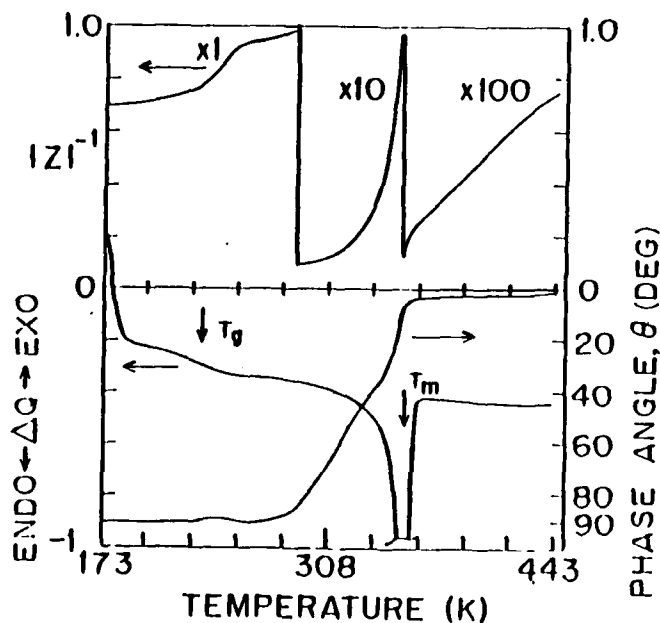


Figure 2. Composite figure showing variation of $|Z|^{-1}$, θ , and ΔQ as a function of temperature at a heating rate of $10^\circ\text{C}/\text{min}$. and measuring frequency of 20 KHz for a sample of $\text{ZnI}_2(\text{PEO})_{16}$.

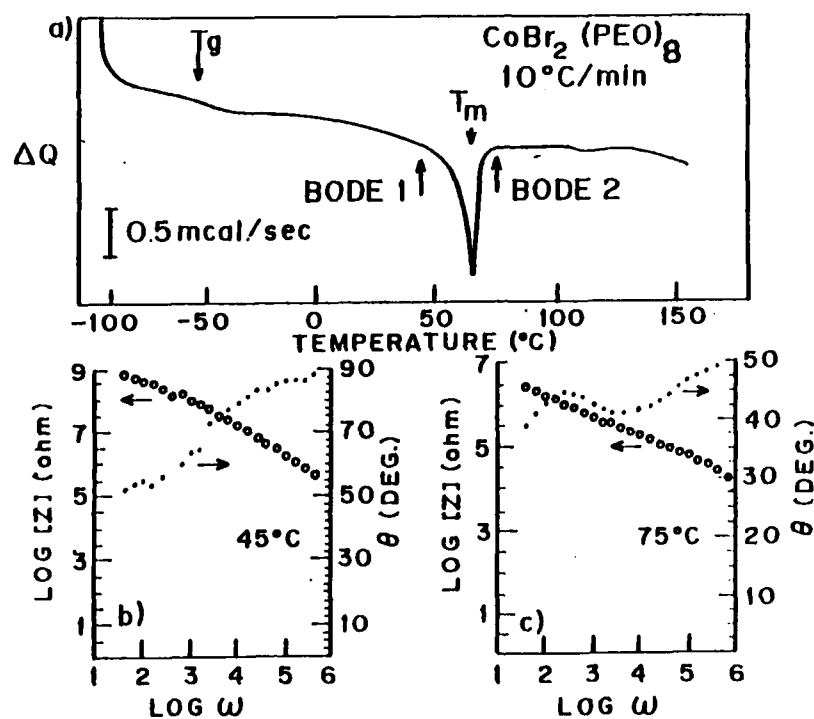


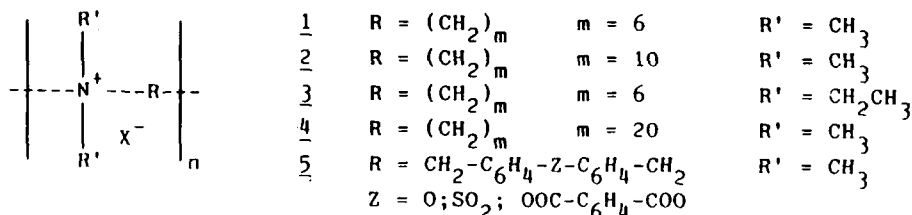
Figure 3. a) DSC scan on a sample of $\text{CoBr}_2(\text{PEO})_8$ at $10^\circ\text{C}/\text{min}$. taken in a combined DSC/DETA cell. b) and c) Bode plots obtained at points 1 and 2 shown in a).

SOLID POLYELECTROLYTES: PROPERTIES OF IONENES

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In contrast to "polymer electrolytes" relatively little is known so far about the solid state properties of "polyelectrolytes", which contain ionic centers and counterions as part of their constitutional repeating (monomeric) units. There are no data available about the influence of ion density on the crystal structure, morphology, thermal and (di)electrical properties of solid polyelectrolytes.

To be able to estimate the possibility of fast ion diffusion as well as other solid state properties in crystalline and amorphous polyelectrolytes we chose poly((dialkylimino)alkylene-salt)s (1-4), which have been described by Dieterich et al.¹⁾ and have been named "ionenes" by Rembaum et al.²⁾, and some aromatic analogues (5).






The ion density in ionenes can be easily adapted by varying the length of the chain R, the size of the side chain R' and the type of the counterion X⁻. For crystal structure investigations low molecular-weight models such as trimers (n=3) have been synthesized.

Results

Usually, the synthesis of the ionenes following the procedures which have been described by Rembaum et al.²⁾ provides for bromide or chloride as counterion, which has to be exchanged in order to introduce different types of counterions. The ion-exchange can be controlled such, that product purities better than 97% (as evidenced by elemental analysis) can be obtained.

The properties of the ionenes strongly depend on the length of the chain R, the side chain length R' and the type of the counterion. In the case of aliphatic chains R the influence of the chain length m can be estimated by comparison of the melting temperatures of various ionene salts, e.g. 1-tos (m=6) m.p. 249°C, with 2-tos (m=10) m.p. 99°C, 1-trif (m=6) m.p. 206°C, with 2-trif (m=10) m.p. 118°C (compare table), indicating the melting temperature to decrease with increasing m. The same is true for different side chain lengths R', e.g. 1-tos (R'=CH₃) m.p. 249°C, with 3-tos (R'=CH₂CH₃) m.p. 119°C, and 1-trif (R'=CH₃) m.p. 206°C with 3-trif (R'=CH₂CH₃) m.p. 98°C (compare table). Obviously, the larger the volume fraction of the organic component in the repeating unit, the lower the melting transition temperature:

Ionene	X ⁻	Calculated			Found			M. p. / °C ^(a)
		C	H	Y ^(a)	C	H	Y	
<u>1</u> -tos		60,17	8,42	10,41 (S)	57,98	8,31	10,18	249
<u>1</u> -trif	F ₃ CSO ₃ ⁻	38,99	6,50	20,57 (F)	38,99	6,62	20,30	206
<u>1</u> -BF ₄	BF ₄ ⁻	44,55	8,35	35,25 (F)	42,56	7,94	30,75	276
<u>1</u> -SbF ₆	SbF ₆ ⁻	26,40	4,95	31,33 (F)	26,37	5,06	30,65	235
<u>1</u> -ZnBr ₄	ZnBr ₄ ²⁻	29,95	5,62	49,86 (Br)	29,93	5,75	50,06	—
<u>2</u> -tos		64,23	9,30	9,01 (S)	61,91	8,86	9,47	99
<u>2</u> -trif	F ₃ CSO ₃ ⁻	46,85	7,81	17,11 (F)	46,72	7,79	17,28	118
<u>2</u> -BF ₄	BF ₄ ⁻	53,18	9,60	28,05 (F)	53,02	9,72	27,97	127
<u>2</u> -SbF ₆	SbF ₆ ⁻	34,31	6,20	27,15 (F)	34,18	6,30	27,40	283
<u>3</u> -tos		62,93	8,87	9,79 (S)	59,32	8,39	9,50	119
<u>3</u> -trif	F ₃ CSO ₃ ⁻	43,28	7,21	18,68 (S)	39,57	6,93	18,26	98

^(a) In parentheses reference element of the counterion.

^(b) Melting temp. by DSC.

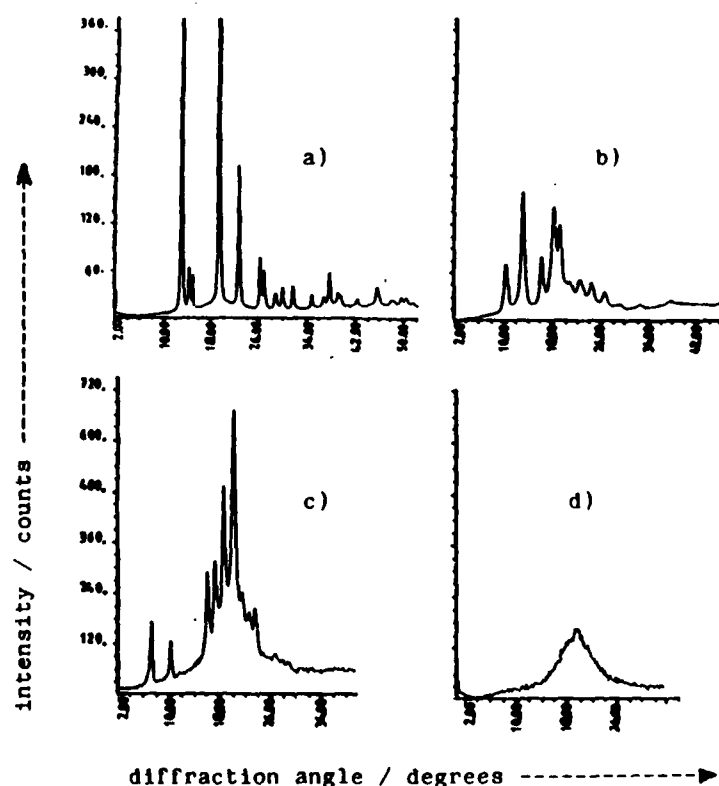
This behaviour is also substantiated by recent results obtained with 4-salts (m=20), which generally exhibit the lowest melting transition temperatures among the ionenes under our investigation.

The high melting transition of 1-BF₄ m.p. 276°C as compared to the relatively low transition temperature of 1-trif m.p. 206°C clearly demonstrates the influence of the nature of the counterion on the thermal properties. However, this influence is largest in ionenes with small organic components, thus with high ion density (m=6), and decreases in ionenes with increasing size of the organic components, thus with small ion density, being minimized in the 4-salt series.

The thermal properties of the ionenes should, however, not be discussed without consideration of the degree of crystallinity and the crystal structures.

Ionenes cover a broad range of morphologically different materials: ionenes with R and R' being small generally appear to be highly crystalline, in some very exceptional cases even single crystalline (polymeric) ionenes have been obtained. With increasing size of R and R' the ionenes become partially crystalline or even amorphous. This can be evidenced by comparing the X-ray diffractograms of the 1-salt series with that of the 2-, 3- or 4-salt series, e.g. 1-SbF₆ (fig.a) with that of 2-SbF₆ (fig.b) and 2-BF₄ (fig.c), with only the latter two exhibiting a halo around $2\theta=20^\circ$, which is typical for partially crystalline polymers.

While the 1-salts usually can be recrystallized from the melt, this is not possible for the 2-salts and 3-salts, so that glassy solids can be obtained. The X-ray diffractogram of glassy 2-BF₄, which was slowly cooled from the melt, typically exhibits only a broad "amorphous halo" (fig.d).



"Trimers" ($n = 3$) have been prepared as models for the polymeric ionenes. Surprisingly, not only the trimers have been grown into single crystals, but also some of the polymeric ionenes, e.g. $\underline{1}$ -ZnBr₄ could be obtained as relatively large single crystals, which are useful for crystal structure investigations.

Dielectric spectroscopy of partially crystalline and amorphous ionenes between 120 and 350°K, and from 10 to 10⁷ Hz reveals the influence of glass and melting transition temperature on both, the dielectric loss and ionic conductivity of the ionenes. In the case of glassy $\underline{1}$ -BrF₄, a glass transition at 310°K was found, with the conductivity (1 kHz) increasing from about 5×10^{-7} Scm⁻¹ at 305°K to about 1×10^{-5} Scm⁻¹ at 320°K.

The ionic conductivity in ionenes must also be discussed in view of ²H-NMR studies on molecular motions a) in interpolymer complexes of ionenes published recently ³), and b) in ionene salts (own measurements), which both indicate large angle conformational deformations being possible also remarkably below T_g in glassy polyelectrolytes.

More details about the (di)electrical properties of ionenes and their aromatic analogues as well as other thermal and optical properties will be presented at the poster.

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LITHIUM/POLYETHER INTERFACIAL INSTABILITY

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INTRODUCTION

The main thrust of recent work on polymer electrolytes for lithium batteries has been towards the synthesis and characterisation of high conductivity material. However, little attention has been paid to the stability of those electrolytes with lithium electrodes, although the resistance of interfacial reaction products may well be the performance-limiting factor, especially in very thin cells [1].

Studies on thick cells of PEO-lithium salts with lithium electrodes operated above room temperature revealed the presence of a passivating layer at the lithium/polymer interface [2,3], which could seriously affect performance. This work is intended to evaluate the effects of interfacial reactions at room temperature between polymer electrolytes and lithium.

EXPERIMENTAL

Nickel tracks were evaporated onto the glass substrates using appropriate masks (Fig. 1a). A solution of polymer in acetonitrile was applied across the contacts by dip coating under an argon atmosphere using PTFE tape as a mask. The solvent was evaporated leaving a thin polymer film (fig. 1b). The lithium electrode was made by vacuum evaporation across the polymer film making a bridge to the nickel track through another mask (fig. 1c). Lithium evaporation was performed using a standard vacuum evaporator housed within an argon atmosphere dry box. An array of eleven such cells each having an effective area of 0.08 cm^2 was fabricated on a single substrate. Complex impedance measurements were made in the frequency range 13 MHz to 5Hz and repeated at various time intervals after the initial fabrication. The following polymers were used for the present study, doped with one LiClO_4 per 8 ether oxygens in each case:

1. PEO (crystalline), Aldrich "M.W. 5,000,000".
2. Oxyethylene-oxyethylene copolymer (amorphous)
(supplied by Dr C. Booth, Manchester University)
3. PPO (amorphous), Hercules Inc. "Parel 58".

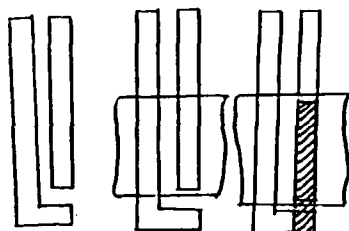
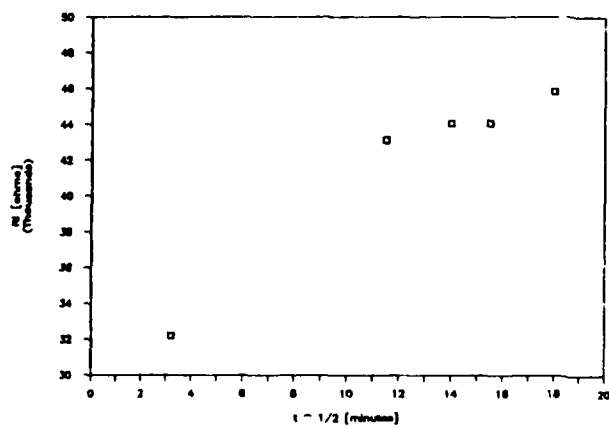
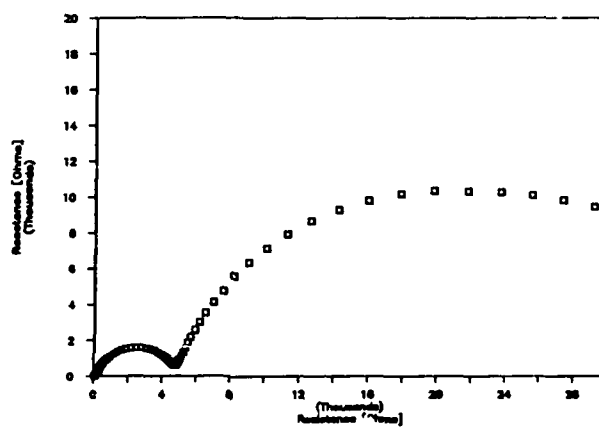


Fig. 1

Cell fabrication steps

Fig. 2

Impedance spectrum of
PEO-LiClO₄ cell.

Fig. 3 $t^{1/2}$ vs R_1

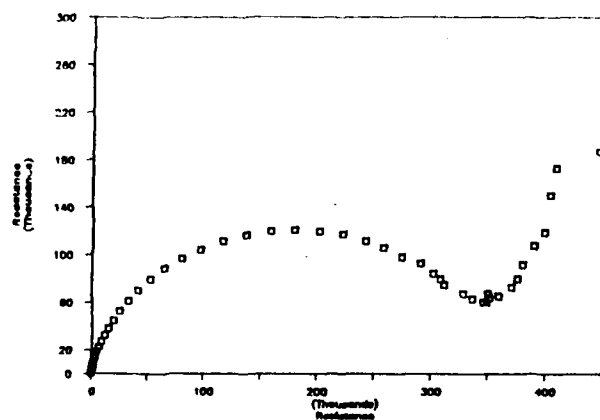


Fig. 4

Impedance spectrum of PPO-LiClO₄ cell.

RESULTS AND DISCUSSION

Fig. 2 shows the impedance diagram obtained for a Ni/PEO - LiClO₄/Li cell. It is evident that there are two distinct relaxation phenomena in this system. From the values of time constants of these relaxations we can deduce that the one at high frequency is due to the PEO and that the one at low frequency is due to an interfacial reaction product.

The thickness of PEO is estimated to be around 4 μm as measured by SEM for one of the cells prepared in the same way. The conductivity of the PEO was calculated from the resistance and the geometric factors, and found to be about 10^{-6} S/cm. (The dielectric constant for PEO is calculated to be about 19 from the relaxation time constant).

The minimum area specific resistance obtained for PEO was about 160 ohm cm^2 - a value which should allow acceptable current densities even for the poorly-conducting PEO at room temperature. The polymer resistance was found to increase slightly with time, presumably due to slow crystallization of the PEO.

The interfacial resistance, however, was found to be much larger than that due to the polymer, and increased appreciably with time (Fig. 3). (The $t^{1/2}$ dependence is a common observation in corrosion phenomena). Assuming the dielectric constant of the interfacial layer to be 10, the thickness of the interfacial layer was estimated to increase from about 20 to 40 \AA and the conductivity was calculated to be about 10^{-10} S/cm.

Fig. 4 shows the complex impedance diagram for a typical Ni/PPD/Li cell. Here the single relaxation has a time constant similar to that of the PEO - Li reaction product, and is therefore assigned to the reaction product of Li and PPD. However, the resistance here is much larger, probably because of a greater thickness, and completely masks any resistance due to the polymer. Considering the dubious purity of the sample, the greater extent of reaction may well have been due to impurities in the PPD rather than the polymer itself.

In the case of the amorphous oxyethylene-oxymethylene copolymer, the lithium film disappeared immediately after evaporation, indicating a very fast interfacial reaction.

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ACKNOWLEDGEMENT

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"OXYMETHYLENE-LINKED POLY(ETHYLENE OXIDE)" ELECTROLYTES

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High-molecular-weight samples of "amorphous" poly(ethylene oxide) have been prepared. The conductivities of electrolytes formed from these materials are comparable with the best values reported for other high-polymer systems.

High-molecular weight poly(ethylene oxide) (PEO) is a good polymer electrolyte, combining useful ionic conduction with satisfactory mechanical properties^{1,2}. However PEO is normally highly crystalline at room temperature and so, since conduction is mostly through the amorphous phase^{1,2}, the polymer has practical application only in high-temperature devices ($T > 80^{\circ}\text{C}$).

The crystallinity can be reduced by incorporating co-units into the poly(oxyethylene) chain. If these units are fairly evenly (but not regularly) spaced along the chain, long oxyethylene sequences are avoided and the melting-point depression is maximised. Indeed the melting points of polymers consisting of linked oxyethylene sequences with narrow distributions of lengths are found³ to be similar to those of their unlinked precursors. This observation provides a basis for the preparation of "amorphous" PEO, the essential pre-requisite being a supply of low-molecular-weight poly(oxyethylene) with reactive end groups and a melting point below room temperature.

Fortunately this requirement is easily met, suitable

starting materials being the readily-available polyethylene glycols (e.g. PEG400, PEG200). These diols can be readily linked by the Williamson reaction, with a dihalomethane as the linking agent. The resulting oxymethylene links are effective in limiting the crystallisation to that of the short oxyethylene sequences⁴.

A short summary of the preparative method is given at the end of this account. The chemistry is straightforward and the preparative methods are those of "bench-top" organic chemistry. Ring formation⁵ is indicated by the low-molecular-weight peak in Fig. 1.

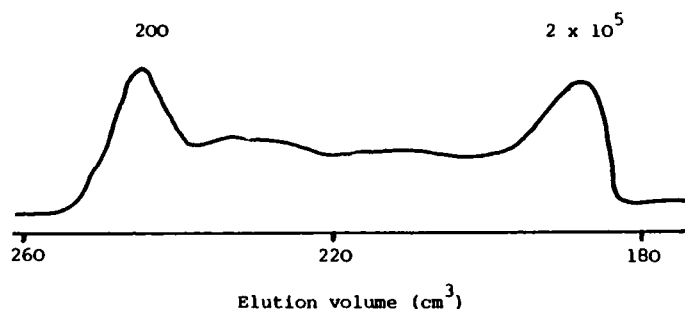


Fig. 1. GPC curves of oxymethylene-linked PEO prepared by use of CH_2Br_2 linking agent. Approximate molecular weights are indicated on the curve.

Materials produced from CH_2Br_2 and PEG400 under suitable reaction conditions are elastomers at room temperature: typically $M_w > 100000$, $T_m = 15^\circ\text{C}$. [Note: $T_m = -10^\circ\text{C}$ for polymer prepared from PEG200]. The glass transition temperature of linear high polymer, $T_g = -65^\circ\text{C}$, is similar to that of conventional PEO. Material produced directly by use of CH_2Br_2 without purification^{4,5}, which contains a

substantial fraction of plasticising rings (see Fig. 1), may have $T_g = -80^\circ\text{C}$. Conductivities (σ) have been determined for pure linear polymers mixed with LiCF_3SO_3 in various proportions. For example conductivities of $\sigma \approx 5 \times 10^{-5} \text{ S cm}^{-1}$ at 20°C and $\sigma \approx 6 \times 10^{-4} \text{ S cm}^{-1}$ at 100°C were found for a polymer produced by use of CH_2Br_2 and PEG400 [$M_w = 200000$, $T_m = 18^\circ\text{C}$, $T_g = -64^\circ\text{C}$] containing optimum salt concentration [O:Li = 25:1]

A comparison of results with conductivities reported for conventional PEO⁶ and for polyphosphazine MEEP⁷ is made in Fig. 2. The effect of crystallisation in PEO is to dramatically reduce σ at temperatures below its melting point ($T_m \approx 70^\circ\text{C}$). By contrast the "amorphous" PEO has a fairly flat curve of σ versus $1/T$, similar to that found for polyphosphazines.

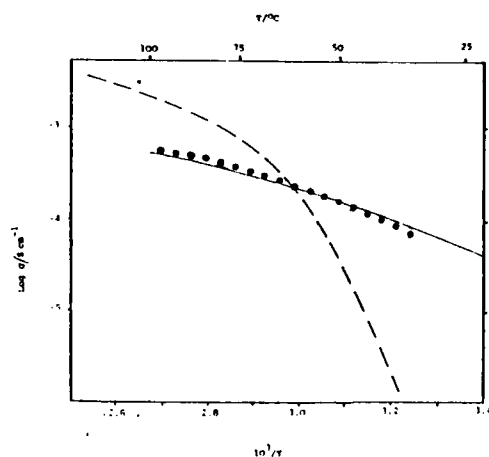


Fig. 2. Log conductivity versus reciprocal temperature for (---) PEO (O:Li, 12:1, LiClO_4), (•••••) polyphosphazine (O:Li, 16:1, LiCF_3SO_3) and (—) oxymethylene-linked PEO (O:Li, 25:1, LiCF_3SO_3).

Preparation of oxymethylene-linked PEO

Finely-ground KOH, chlorobenzene and excess dibromomethane were mixed under nitrogen in the dark at room temperature. PEG400 was added slowly and the reaction mixture was stirred for 16 hrs. After filtration and washing, the product was examined by GPC and found to contain a wide distribution of molecular weights (see Fig. 1). The material was fractionated by use of a toluene/heptane mixture. The high polymer so isolated was used for conductivity measurements. Details of the preparation and purification, including molecular characterisation of the product, can be found in references 4 and 5.

Acknowledgments

We are pleased to acknowledge helpful discussions with Dr. R.H. Mobbs (Manchester University) and Dr. J.R. Owen (Salford University).

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NEW ELECTROCHEMICAL CELLS BASED ON DIVALENT POLYMER ELECTROLYTES

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Ionically conducting polymers consisting of a complex between a metal salt and poly(ethylene oxide) (PEO) offer a number of advantages over other solid electrolytes, with regard to their possible use in advanced solid-state electrochemical devices. Interesting results on these electrolytes have been reported by several workers (1-3).

We have prepared and studied polymeric complexes of poly(ethylene oxide) (PEO) with salts of zinc, copper and silver (4). It was concluded that some of the studied compounds are good solid electrolyte materials in view of their high ionic conductivity, their low electronic conductivity, and their chemical compatibility with high energy density electrode materials.

Experiments have been carried out on cells utilising electrolytes, the conductivities of which are at the lower limit of values acceptable for batteries for present day use. The choice of type and amount of salt used in these electrolyte films was dictated by a systematic study of factors affecting conductivity, the results of which have been published elsewhere (5,6). The performance of the cells was further limited by the use of a simple casting technique to form the composite (polymeric electrolyte matrix/active constituent) cathode; it has since been shown that significant improvements result from modifying the casting technique (7,8). Despite these limitations, the currents drawn were modest but adequate for certain practical devices. An optimised choice of anion and stoichiometry for a given divalent cation species can lead to an improvement of two orders of magnitude in conductivity (5), and a concomitant improvement in cell performance would be anticipated.

Mg/PEO_{1.5}:Mg(SCN)₂/(45% TiS₂, 50% PEO_{1.5}:Mg(SCN)₂, 5% acetylene black) test cells: The test cells exhibited an open circuit

voltage of 1.7 V at 30 ± 1 °C. The test cells were discharged at a constant load at 1 mΩ until apparent exhaustion of active cathode material had occurred. A current of 1 μA could be maintained for 1000 hours and a slightly lower current could be sustained for a further 2000 hours or so. Additionally, test cells were used to supply the power to an LCD clock (requiring >5 μA at >1.2 V) for periods of two weeks at ambient temperatures as low as 15 °C.

M/PEO₁₅:MX₂/(45% TiS₂ or V₂O₅, 50% PEO₁₅:MX₂, 5% acetylene black) test cells: These test cells included Mg, Mg(SCN)₂; Mg(ClO₄)₂; Zn, Zn(ClO₄)₂ anode/electrolyte combinations. For Mg/Mg(SCN)₂/TiS₂, a current of 0.5 μA could be sustained for 400 hours. For Mg/Mg(ClO₄)₂/V₂O₅ cells, a current of 1 μA could be maintained for the same time. For Zn/Zn(ClO₄)₂/TiS₂, a current of 0.5 μA could be sustained for 300 hours, but if TiS₂ were replaced by V₂O₅ the same current could only be maintained for 100 hours.

M/PEO₁₅:M'(SCN)₂/(45% TiS₂ or V₂O₅, 50% PEO₁₅:MX₂, 5% acetylene black) test cell: Here the anode metal differed from the divalent cation in the electrolyte. For test cells involving a Zn anode with a PEO₁₅:Mg(SCN)₂ electrolyte and a V₂O₅ cathode, 0.5 μA could be maintained for 120 hours. A rather better performance was obtained from the combination Mg anode, PEO₁₅:Ca(SCN)₂ electrolyte and TiS₂ cathode; 0.8 μA could be sustained for 1000 hours. In general, for these "mixed" systems, many of which did not meet our minimum performance specifications (0.5 μA, 100 hours), Mg anodes always outperformed Zn or Al anodes in conjunction with TiS₂ cathodes, whatever salt was used. This even included systems for which the divalent cation in the salt corresponded with the anode material.

Acknowledgements

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ANIONIC TRANSPORT IN POLYMERIC SOLID ELECTROLYTES

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Initiated by the pioneering works of Armand et al (1) in 1978, solid polymeric electrolytes have been the subject of brisk researches owing to their potential use in high energy-density batteries at temperatures upto 423 K. The polymeric substances studied are mostly the polyethers like polyethylene oxide (PEO), polypropylene oxide (PPO) etc. Only a few papers have appeared on other types of polymers like polyimines (2,3) or polyphosphazenes (4,5). Alkali and alkaline earth metal complexes of polymers based on polyethers can be prepared easily by dissolving the salts (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{++} , Mg^{++} etc. with counter ions like halides, perchlorate, fluoborate and triflate (CF_3SO_3^-) in molten polymers under anaerobic conditions. Extensive studies of these materials have been made during last decade with respect to their structures (by x-rays, EXAFS), stoichiometries (chemical, DSC), phase studies, kinetic studies, transport studies, theory of transport in elastomeric phase (FVT, DBP theories), mechanism of ionic transport, viscoelastic studies etc. The most useful property of these materials is their high ionic conductivity in the elastomeric phase above the glass transition temperature. The molecular mechanism of the ionic conduction process is not yet fully understood. A mechanism of conduction of cations through the polyethers have been advanced (6) on the basis of polyhelical structure of the matrix which supplies lone pairs from oxygen atoms necessary for the formation of the conducting pathway.

Careful determination of the transport number of the ions in such polymeric matrix has now revealed that contrary to earlier belief that the cations are the sole charge carrier, the anions of the alkali metal salts also contribute significantly to the process. In fact, in some cases, the anions are the more important charge carrier. However, for practical application of a high energy-density battery employing polymer solid electrolyte, it is mandatory to have the cationic transference number as close to unity as possible over the temperature range of operation of the cell.

Transference number of the cations and anions in polymeric solid electrolytes have been measured by different workers using a variety of techniques. These include the classical Tubandt procedure (7), complex impedance spectroscopy (8), T_2 relaxation time in NMR spectroscopy (9), chronoamperometry (10), polarisation studies (5, 11), radioactive tracer diffusion coefficient measurements (12) and PFG NMR measurements of diffusion coefficients (13). The application of these different methods is necessitated by the widely divergent values of transport numbers derived from them such that unambiguous and universally acceptable values could not be ascertained up till now. For example, cationic transference number ranges from 0.03 to about 0.95. The reason for such wide variation is not clear.

The fact that both cations and anions are responsible for charge transfer through the polymeric solid demands a mechanism of the transport of both types of ions in the elastomeric phase. It is now definitely known that fully saturated polymer-metal salt complexes with low O:M ratio leads to crystalline compounds which are almost non-conductors. But in the elastomeric phase, particularly above the glass transition temperature, the crystals dissolve in excess of the uncomplexed polymer to result in unsaturated complexes. Under this condition, the cations are subjected to the field of available lone pairs from the oxygen (or electronegative element) of the excess polymers. In the dynamical medium, these neighbouring electron pairs can accept the cation and these may hop from place to place along the polymeric strands. While this is a reasonable microscopic picture of cation migration, the mechanism of transport of the anions remain unexplained and usually it is assumed (without much reason) that the anions are completely free to move in the polymeric matrix.

It seems reasonable to consider that both the cations and the anions are complexed by the polymeric solid, the latter behaving as a multidentate ligand. The cation is 'coordinated' by the electron pairs of the polymer and this 'electronation' of the cation is the reason for its solvation in the polymer. If the strength of the 'electronation' is small the solubility of the salt in the polymer will be low. On the other hand, a very strong 'electronation' of the cation will hamper its migration through the polymer

because the possibility of bond breakage (and subsequent bond renewal) necessary for migration will be small. The anions will similarly interact with the hydrogens of the polymer backbone to form hydrogen (proton) bond and may be considered as 'protonated'. Such bonds are normally very weak so that their formation and breakage may take place without much involvement of energy. They are, therefore, relatively free to move through the electrolyte.

For migration through the polymer the cations need a continuous electron path. This is supplied by the periodic disposition of the electron pairs associated with the electronegative element of the polymer. However, for the anions, the required continuous 'proton path' will be provided by the periodic disposition of the hydrogen atoms of the organic backbone of the polymer. With these ideas the variation of mobility of different types of anions through the polymer as well as the dependence of mobility of anions with temperature and pressure can be rationalized.

The variation of the mobility of the anions depends on intrinsic factors like 1) hydrogen bonding ability, 2) size and 3) polarity of the anion and extrinsic factors like temperature and pressure.

The hydrogen bonding ability or 'protonation' of the anion is directly related to its solubility. A strong protonation will increase the solubility at the cost of the mobility through the polymer. It appears that too small a size of the anion will cause it to rattle in the interstices and prevent its motion through the continuous proton path although the higher ionic potential would ensure its greater solubility in the polymer. However, diffusive motion will be more allowable for anions with small volume and the opposite will hold for those with larger size irrespective of their greater mobility along continuous proton path. The polarity of the anion is by far the most important factor in deciding the ultimate anion mobility. Even if the size and the 'protonation' ability of the anion is favourable for migration, its dipolar character might cause it to form clusters and prevent its easy motion. They will also hinder the motion of cations by forming ion-pair. Thus a dipolar anion of moderate size containing atoms capable of protonation will render it less mobile than a non-polar anion. Triflate ion satisfies these characteristics and Li-triflate is, therefore, widely used in polymer based lithium storage batteries. This is

however, not an ideal choice particularly at higher temperature, where the anion shows considerable mobility.

An increase of pressure brings the polymer backbone closer to each other so that for a given size of the anion, formation of closer proton path will result in greater mobility for an anion like ClO_4^- , than a dipolar anion like thiocyanate or triflate. Increase of temperature will increase in general the mobility of all types of anions.

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IMPEDANCE AND OTHER STUDIES
OF ZINC POLYMERIC ELECTROLYTES

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Poly(ethylene oxide) in conjunction with zinc salts can be used to form electrolyte films of $\text{PEO}_x:\text{ZnX}_2$ which are analogous to the better known Li polymeric electrolytes. Both Li and Zn systems contain spherulites. Unlike the majority of Li electrolytes (1,2), the Zn based materials usually contain only one type of spherulitic region, corresponding to PEO; no high-melting complex appears to be present in these cases. They can be used in conjunction with Zn electrodes (which are substantially less chemically reactive than Li) for low current density power source and other applications (3).

Figures 1a and 1b show typical results for differential scanning calorimetry experiments for both a Li and a Zn polymeric electrolyte. The following features are observed :- (i) a low temperature step at T_g ; (ii) an endothermic and fairly sharp peak corresponding to pure PEO melting; (iii) for the Li trace only, a broad high-temperature peak arising from the melting of polymer-salt complex.

By contrast figures 2a and 2c show that for the $\text{PEO}_{20}:\text{ZnBr}_2$ system there is evidence for the presence of high melting polymer-salt complex. As for Li systems (4) the melting point of the complex is composition dependent. The sample used in figure 2 was subjected to the thermal history shown in figure 3; the behaviour is summarised in table 1. The T_g indicates the presence of an amorphous phase and the broad peak at a higher temperature than the PEO endotherm confirms the presence of the complex; there is a salt balance between these two phases. After natural cooling of the melt to room

temperature, followed by quenching to -90°C the heating cycle was repeated, giving rise to figure 2b. Here, the peak due to the complex is absent because there was insufficient time for crystallisation. After prolonged storage it can be seen from figure 2c that the amount of complex has increased and its melting point is higher; there are concomitant changes in the temperature and height of the T_g step. The contrast between the behaviour of ZnI_2 (no complex) and ZnBr_2 (complex) electrolytes may be strongly influenced, not only by the anion, but also by the preparation conditions (which differed for the two samples).

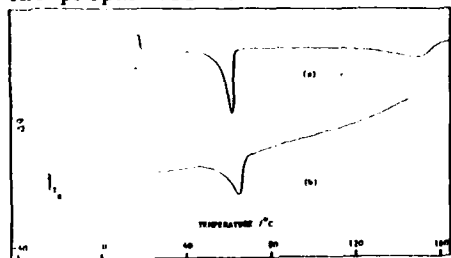


Figure 1. DSC traces for

(a) $\text{PEO}_7:\text{LiCF}_3\text{SO}_3$; (b) $\text{PEO}_{20}:\text{ZnI}_2$ fig.2 sample of $\text{PEO}_{20}:\text{ZnBr}_2$

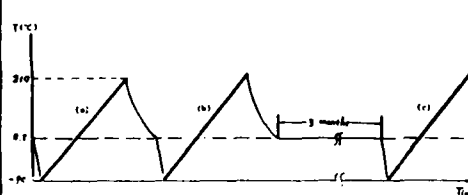


Figure 3. Thermal history for the

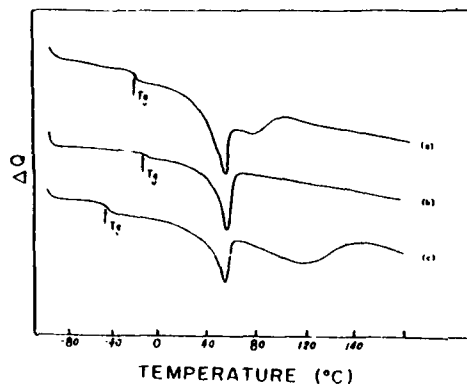


Figure 2. DSC traces for

fig.2 sample of $\text{PEO}_{20}:\text{ZnBr}_2$

	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$) (Pure PEO)	T_m ($^{\circ}\text{C}$) (Complex)
First heating (a)	20	60	70-90
Reheating immediately (b)	0	60	
Reheating after standing at RT for 3 months (c)	-40	60	60-130

Table 1. Thermal data for the

fig.2 sample of $\text{PEO}_{20}:\text{ZnBr}_2$

The results from other studies, such as SEM/EDX and variable temperature polarising microscopy, on Zn polymeric electrolytes will be presented at the symposium.

Electrolyte conductivities are obtained from the extrapolation of the high frequency end of the 'interphase region' of the impedance plot. (It is worth noting that the age of the PEO used to make the film can affect the conductivity of an electrolyte film of given stoichiometry by a factor of ≈ 100 .)

Normally the conductivity variation with temperature is depicted on an isoplethic ('Arrhenius') plot. This variation is accompanied by a change in the appearance of the impedance plots (Figure 4), resulting from the low and high frequency limits of whatever instrumentation is used. CPA elements find particular application in the equivalent circuits of these, and other, polymeric electrolytes.

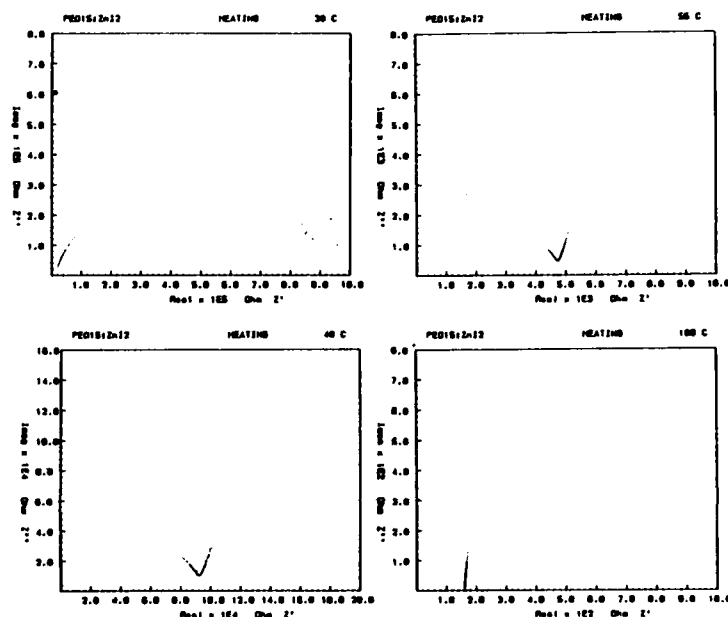


Figure 4. Variation of impedance plots with temperature for the system $\text{PEO}_{15}:\text{ZnI}_2$.

The transport number of Zn^{2+} in these films has been measured from the impedance spectrum using Zn electrodes; for example, $\text{PEO}_{15}:\text{ZnI}_2$ at 120°C , $t^+ = 0.19$, and at 100°C , $t^+ = 0.23$. Unlike totally amorphous systems these results cannot be extrapolated to room temperature because of the intervening morphological changes. The classic method [5] cannot be used at room temperature because not all of the three items of information required lie within the accessible frequency range. Watanabe's use [6] of the d.c. limit overcomes this limitation.

A preliminary comparison of Zn and other divalent salt electrolytes is shown in figure 5. The conductivities of the chlorides are at least an order of magnitude lower than those of

the corresponding perchlorates; there is a significant dependence on cation type for the chlorides but not for the perchlorates. It can be inferred that, provided the morphology is similar, the transport number of the anion is greater in the latter case. It is therefore possible to obtain indications of transport number from experiments using blocking electrodes.

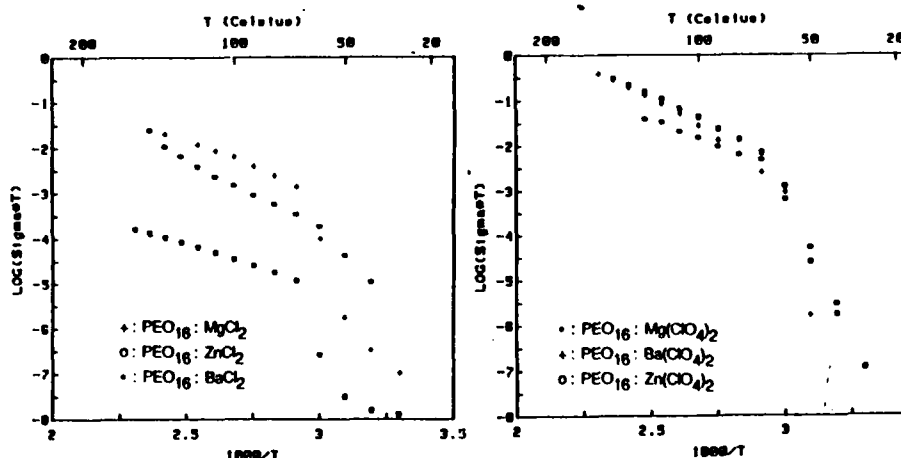


Figure 5. Isoplethic conductivities for divalent polymeric electrolytes; (a) $\text{PEO}_{16}:\text{MCl}_2$, (b) $\text{PEO}_{16}:\text{M}(\text{ClO}_4)_2$.

Acknowledgement:

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**Proton Conduction in Linear Poly(ethylenimine)-Sulfuric Acid
and -Phosphoric Acid Systems**

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Solid electrolytes that exhibit high proton conductivity are of great interest as the electrolytes suitable for use in batteries, fuel cells, and electrochromic display devices. Among the reported organic proton conductors have been triethylenediamine-sulfuric acid composites. In contrast to Nafion films etc., it remains proton-conducting in the absence of imbibed water.¹ Linear poly-(ethylenimine)(PEI), structurally the simplest secondary amine polymer, seems to be a suitable building block of the polymeric proton conductors with above characteristics. We now report some behavior of PEI-sulfuric acid, and PEI-phosphoric acid systems.

EXPERIMENTAL

PEIs (Mw:(L), 5×10^4 ; (H), 1.9×10^5) were obtained as reported elsewhere.² The PEI was weighed after drying under vacuum at 100 °C for 1 day and dissolved in absolute methanol. PEI-H₂SO₄ as well as PEI-H₃PO₄ systems with various degrees of neutralization (acid/EI unit = 0-1) were prepared by adding the calculated weights of concentrated sulfuric acid (>95%) or phosphoric acid (>85%) to the methanol solutions of PEI and stirring at room temperature for 1 day. As long as the acid/EI mole ratio was less than 0.3, no precipitation occurred. When such solutions were cast onto PTFE dishes under N₂ atmosphere, amorphous, hygroscopic polyelectrolyte films were obtained. Their glass transition temperatures (T_g) were below room temperature. The PEI-H₃PO₄ films were mechanically too weak to deserve conductivity measurements.

Precipitation took place when the acid/EI ratio exceeded 0.3. The precipitates were filtered, and dried under vacuum for several days. The solids were crystalline according to their X-ray diffractions; but neither T_g's nor melting points T_m's were observed by DSC below 180 °C where thermal decomposition intervened.

The samples for conductivity measurements were prepared as disks (12 mm in diameter and 0.3 mm in thickness) by pressing the cast films at 100°C (film samples), or by pressing (30 KPa) or rubber-pressing (40 GPa) the precipitated powders at room temperature (pellet samples). The proton conduction through such samples was confirmed by observing the emf's of the hydrogen gas concentration cells constructed with the samples as the electrolytes. The ac conductivities were measured between a pair of stainless steel electrodes at various temperatures under vacuum on a Yokogawa-Hewlett Packard 4192A Impedance Analyzer over a frequency range of 5 Hz-13MHz.

RESULTS AND DISCUSSION

PEI-H₂SO₄ Films. Typical complex impedance plots are shown in Fig.1. The temperature dependences of bulk conductivities of film and pellet samples of PEI-H₂SO₄ are shown in Fig.2. The amorphous films exhibit curves of the WLF type above their glass transition temperatures; the ionic hopping may be cooperative with the segmental motions of PEI. A conductivity maximum arose in Fig.3 at a low H₂SO₄/EI. The addition of sulfuric acid initially gives rise to an increase in the number of ionic carriers, but the ionic interactions among PEI chains get stronger as the degree of neutralization increases. As evidenced by the large elevation (from 250 to 298 K) of T_g measured by DSC, the systems become more and more viscous, and the ionic mobility decreases significantly.

A very simplistic consideration of the acid-base reactions involved can lead to Fig.4, which shows how much of a designated species will be formed when a certain fraction of sulfuric acid is added to a mole of EI repeat unit. The compositions of the film samples belong to region I of Fig.4. The proton conduction is presumably controlled by hopping

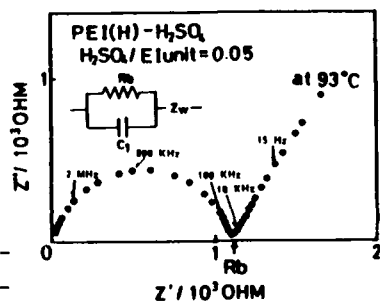


Fig.1 Typical complex impedance plots for a PEI-H₂SO₄ film sample.

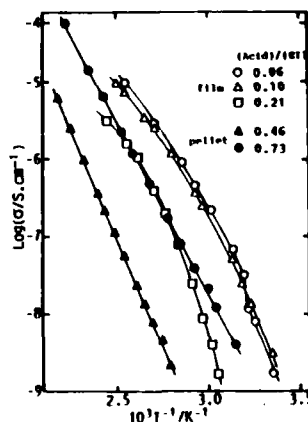


Fig.2 Temperature dependence of electrical conductivity of PEI-H₂SO₄ films and pellets.

of protons from the immonium nitrogens to the unprotonated imino nitrogens; reasonable numbers of not only protonated but also unprotonated EI units seem necessary.

PEI-H₂SO₄ Pellets. The pellets made from the crystalline precipitates were not hygroscopic. Fig.2 shows that the temperature dependence of their ionic conductivity was of the Arrhenius type. Moreover, as the right half of Fig.3 indicates, the conductivity increased rapidly as the degree of neutralization increased; the mechanism of proton migration seems quite different from that in the films.

We can see from region II of Fig.4 that, to the first approximation, the number of protonated EI units becomes constant and the unprotonated imino nitrogens become unavailable as proton sinks at a high degree of neutralization. The proton interplays among the hydrogen-sulfate and sulfate ions, which coexist in the framework of protonated PEI chains, have to be dominating the proton conduction. A reservation must be made, however, concerning the role played by the PEI chains. It is known that some 30 % of the imino nitrogens of branched PEI remain unprotonated even at pH = 2 in aqueous solution because of the Coulombic repulsion from the already protonated sites on the same polymer chains.³ If similar unprotonated nitrogen sites are present in our pellets, they also should provide the proton hopping sites.

PEI-H₃PO₄ Pellets. In contrast to PEI-H₂SO₄, the precipitates here were very hygroscopic and their assaying was difficult. The DSC diagram of the dried precipitates, especially with $(\text{H}_3\text{PO}_4)/(\text{EI}) < 0.5$, were irreproducible; a small peak often appeared near 60 °C, but sometimes it did not. This sort of structural instability appears to be reflected in the nonlinear Arrhenius plots in Fig.5. Despite of this difficulty, the pellets were by ca. 2 orders of magnitude more conductive than PEI-H₂SO₄ of a similar acid/EI ratio if compared at a common temperature.

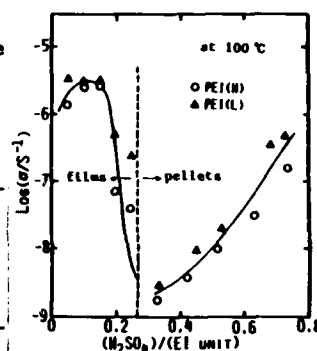


Fig.3 Composition dependence of electrical conductivity of PEI-H₂SO₄ at 373 K.

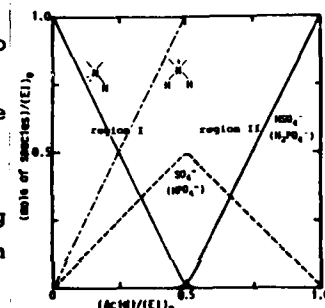


Fig.4 Relative amounts of chemical species present in PEI-H₂SO₄ or PEI-H₃PO₄, a simplified picture.

As Fig.6 indicates, the gross feature of the dependence of conductivity on composition was similar to that of PEI- H_2SO_4 pellets. If we could assume that each protonated site of PEI has a Brønsted pK_a of ca. 9 (a reasonable value for a monomeric secondary amine); phosphoric acid, whose pK_{a1} , pK_{a2} and pK_{a3} are 2.15, 7.20, and 12.35, respectively, should act perfectly as a dibasic acid. Then Fig.4 would again account for the relative amounts of chemical species present in a pellet; here, of course, HPO_4^{2-} and $\text{H}_2\text{PO}_4^{-}$ anions take the places of SO_4^{2-} and HSO_4^{-} , respectively. Proton transit through the arrays of co-existing HPO_3^{2-} and $\text{H}_2\text{PO}_3^{-}$ anions is probably responsible for the proton conduction. Nevertheless, deviation of the simplified picture of Fig.4 from the reality must be more serious than in the case of PEI- H_2SO_4 . Namely, as the degree of protonation of a PEI chain increases, the pK_a of a protonated site in such a chain can become comparable to or even lower than that of HPO_3^{2-} .⁴ Participation of PEI nitrogens to the proton relay cannot be totally discounted even when $\text{acid}/(\text{EI})_0 > 0.5$.

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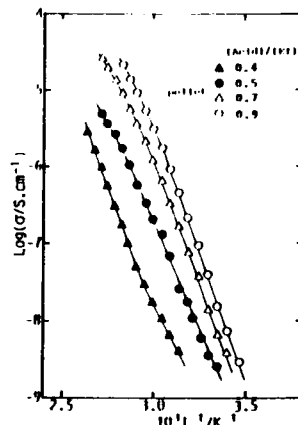


Fig.5 Temperature dependence of electrical conductivity of PEI- H_3PO_4 pellets.

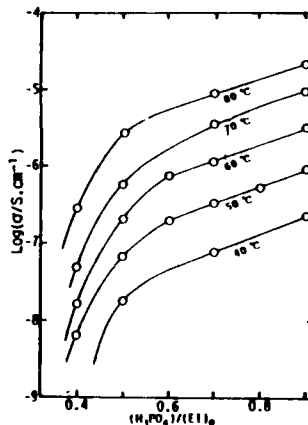


Fig.6 Composition dependence of electrical conductivity of PEI- H_3PO_4 pellets.

A MIXED-SALT POLYETHER ELECTROLYTE : $P(EO)_4(LiCF_3SO_3)_{0.5}(NaI)_{0.5}$

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INTRODUCTION

A study by Moryoussef¹ on the conductivity of PEO/alkaline-earth salt complexes revealed the interesting result that the mixing of salts had a noticeable enhancement on conductivity i.e. a $PEO_{16}(CaBr_2)_{0.5}(CaI_2)_{0.5}$ complex had a greater conductivity than either of the pure $PEO_{16}(CaX_2)_1$, $X = Br/I$, complexes. Although not verified experimentally, it was suggested that this was due to a plastifying effect which favoured the formation of an amorphous phase at the expense of the crystalline phase.

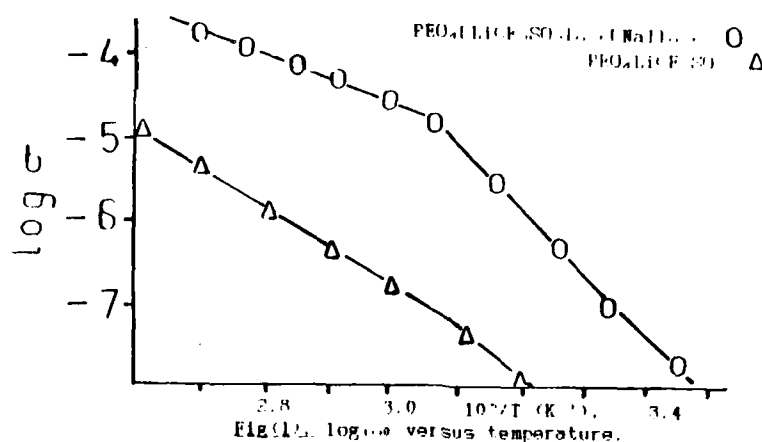
In this paper we present conductivity and nmr results for the mixed-salt polyether electrolyte $P(EO)_4(LiCF_3SO_3)_{0.5}(NaI)_{0.5}$. Attention is given to the modified conductivity and nmr behaviour of the mixed system in comparison to $P(EO)_4LiCF_3SO_3$ and is discussed in terms of the increased topological disorder introduced when more than one salt is present.

EXPERIMENTAL

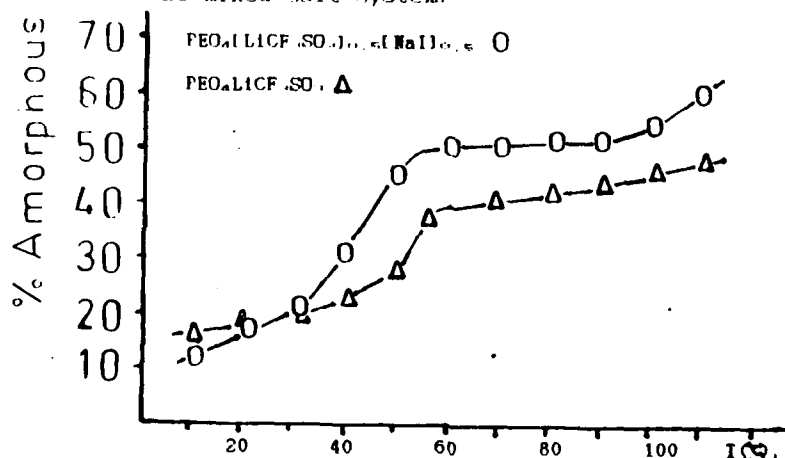
$P(EO)_4$ MWt 4×10^5 (Aldrich Ltd.), NaI (Aldrich Ltd.), $LiCF_3SO_3$ (3M Ltd.) were dried and the required compounds formed by the ball-mill technique². Films were hot-pressed and their conductivity determined by a.c impedance methods³. Samples for nmr were sealed under vacuum and analysed at 50MHz by the Free Induction Decay (FID) / Spin-Echo technique pioneered by Berthier et al⁴ where short T_2 FIDs were associated with crystalline polymer or immobile salt species, and longer T_2 FIDs with amorphous polymer or mobile salt species.

RESULTS/DISCUSSION

Fig.(1) shows the plot of $\log_{10}\sigma$ versus $1/T$ for the mixed-salt system $P(EO)_4(LiCF_3SO_3)_{0.5}(NaI)_{0.5}$. Compared with the available data^{1,2,5,6}, the σ vs. temperature profile shows a marked improvement on that of $P(EO)_4LiCF_3SO_3$ and a slight improvement on that of $P(EO)_4NaI$. Fig.(2) shows plots of the percentage amorphous content for both the mixed-salt and $LiCF_3SO_3$ complexes vs. temperature, as determined by the nmr technique. It is apparent from the figure that Moryoussefs' contention of an increased amorphous phase when salts are mixed is vindicated here, with the mixed-salt system showing 7-10% more amorphous character at most temperatures. Also interesting is the close

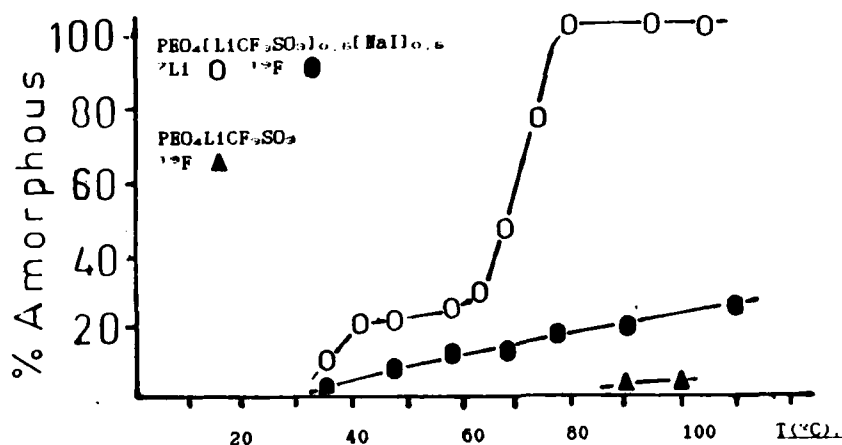


similarity between the conductivity and percentage amorphous profiles for the mixed salt system.



Given that analysis of the relevant FIDs can yield similar information for the ^7Li (cation) and ^{19}F (anion) nuclei as it does for ^1H , data was also taken for those nuclei and their percentage amorphous (or mobile) component calculated vs. temperature for both the mixed-salt and pure LiCF_3SO_3 systems (fig. (3)).

(a) ^{19}F Signal: The $\text{PEO}_4\text{LiCF}_3\text{SO}_3$ fluorine signal was found to be single component, short T_2 ($\approx 30\mu\text{s}$), over most of the temperature range until above 90°C where a small amount ($\approx 4\%$) of long T_2 component was observed. In contrast, the mixed-salt system showed a much larger mobile fraction over the entire temperature range, rising monotonically to $\approx 24\%$ of the total signal at 110°C .

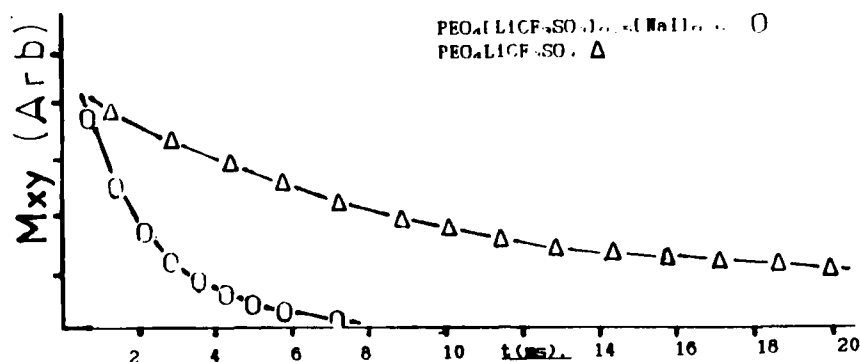


Fig(3). %Amorphous ^7Li and ^{19}F versus temperature.

(b) ^7Li Signal; Like the ^{19}F signal in $\text{P}(\text{EO})_4\text{LiCF}_3\text{SO}_3$, the ^7Li FID was found to be single-component short T_2 ($\approx 120\mu\text{s}$) over the entire temperature range, with no long T_2 (or mobile) component observable. In the mixed system the striking observation was two-component behaviour (short and long T_2) with the appearance and growth of a long T_2 signal near the onset of the region of enhanced conductivity in the σ vs. temperature plot. This mobile component was found to grow rapidly with temperature and by 78°C (where all the $\text{P}(\text{EO})_4\text{LiCF}_3\text{SO}_3$ signal was still short T_2) the ^7Li FID was observed to be one-component long T_2 , suggesting that all lithium cations were now mobile in the system.

The results presented so far suggest that the mixed-salt system contains more charge carriers i.e. mobile anions and cations (fig. (3)), in a more extensive amorphous polymer phase (fig. (2)) than the equivalent $\text{P}(\text{EO})_4\text{LiCF}_3\text{SO}_3$ material. This in turn would immediately explain the enhanced conductivity of the mixed relative to the single salt system and may be considered to be a result of the topological disorder induced into the system by the mixing of salts and hence ion size and type.

Further evidence was gained by estimating the T_2 relaxation times for ^1H (amorphous chain) signals from the decay of the transverse magnetization (fig(4)). T_2 values (considered a probe for chain mobility) for the mixed salt were found to be consistently less than the single salt at all elevated temperatures ($>60^\circ\text{C}$) i.e. at 80°C the $\text{P}(\text{EO})_4\text{LiCF}_3\text{SO}_3$ T_2 value was typically 10ms whereas the mixed-salt was much less at around 2ms, implying that whereas the larger concentration of mobile ions in the amorphous



Fig(4). Decay of the ^1H transverse magnetization versus time.

phase of the mixed salt system can give a larger conductivity than the single salt, they also tend to raise the microscopic viscosity of that phase, probably by networking the system with transient cross-links.

CONCLUSIONS

The mixed salt polyether $\text{P}(\text{EO})_4(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$ has been shown to have a larger amorphous phase content, an increased mobile salt content, and a superior conductivity to that of the equivalent $\text{P}(\text{EO})_4\text{LiCF}_3\text{SO}_3$ system. The effects are considered to arise from the topological disorder introduced into the system by the mixing of salts.

A more detailed treatment, including data for the mixed-salt electrolyte $\text{P}(\text{EO})_4(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$, and discussion of the ion-polarisation effects present in these systems, will be presented elsewhere.

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DSC, Electrical Conductivity, and NMR Studies
of Salting-out Effects in PPO Complexes

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Poly(propylene oxide) (PPO) is known to form amorphous ion conducting complexes with alkali metal salts.^{1,2} Previous studies of PPO complexed with LiClO_4 have shown that large scale segmental motion of the polymer chains is principally responsible for ionic transport², in general agreement with the results of a wide array of recent investigations. The present study concerns related work on $\text{PPO}:\text{NaI}$ and $\text{PPO}:\text{KSCN}$ complexes. In particular, it is observed that these materials exhibit behavior similar to that of previously investigated PPO complexes, however, they become unstable at moderate temperatures ($<100^\circ\text{C}$). As will be discussed, the instability is manifested ultimately by the separation of the salt from the polymer.

We have performed differential scanning calorimetry (DSC), electrical conductivity and ^{23}Na nuclear magnetic resonance (NMR) measurements on PPO_8NaI , both in vacuum (or ambient pressures) and at elevated pressures (up to several kbar). In addition, DSC and conductivity data for PPO_8KSCN are presented.

The host material studied was Parel 58 (Hercules, Inc.) elastomer which is a sulfur-vulcanizable copolymer of propylene oxide and allyl glycidyl ether. As the primary constituent is propylene oxide, the material will be referred to throughout this paper as PPO. The DSC results for PPO_8NaI are shown in Fig. 1. Results for uncomplexed PPO are included for comparison. It is

clear that the complexed material is highly amorphous in that it exhibits a strong glass transition with a "central" T_g of about 6°C . (The "onset" T_g is about 0°C and the "end" is at about 12°C .) Consequently, T_g is about 68°C higher than for the uncomplexed material for which the "central" glass transition temperature is about -62°C as shown in Fig. 1c. An increase in T_g with the addition of salt to PPO is well known phenomenon².

In addition, in the DSC studies for PPO_8NaI , a strong, sharp endothermic event is observed at about 100°C . In order to obtain information concerning this feature, the material was annealed at 175°C , quenched to -140°C as rapidly as possible in situ, and the DSC studies repeated. Typical results for the quenched material after anneal at temperatures above 140°C are shown in Fig. 1b. In all cases, a strong glass transition typical of uncomplexed PPO is observed. In addition, there is a high temperature exothermic event followed by an endotherm. Similar behavior has been observed for $\text{PPO}_8\text{NaClO}_4$ where it was concluded that the high temperature endotherm is due to the salt coming out of the polymer, i.e. "a salting out" effect.³ The primary evidence is that only the glass transition due to uncomplexed PPO is observed after quenching from temperatures above that of the sharp endotherm. Further, the material exhibits the original behavior (Fig. 1a) after allowing the sample to sit at room temperature overnight, i.e. the salt redissolves in the polymer. Salting-out has been observed spectroscopically for PPO containing NaSCN .⁴

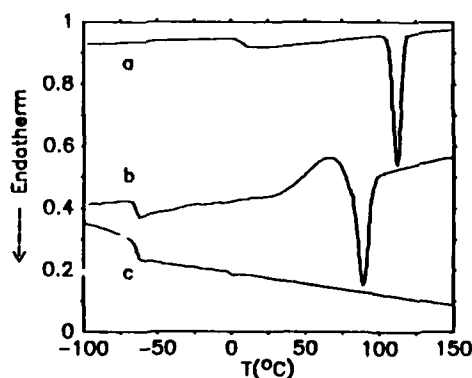


Fig. 1

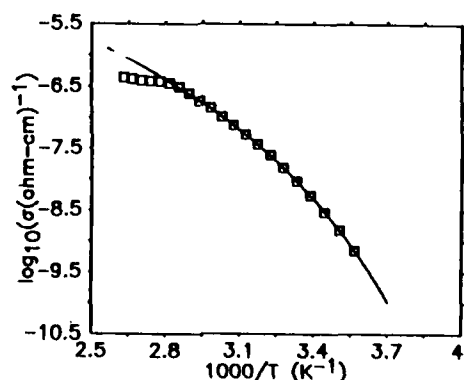


Fig. 2

In order to gain further evidence for the salting-out effect, electrical conductivity studies were performed. (It was not possible to perform such studies for $\text{PPO}_8\text{NaClO}_4$ as the salting-out temperature was outside the range of the conductivity apparatus.) The results are shown in Fig. 2. It is seen that the electrical conductivity begins to deviate from its lower temperature behavior at about 85°C .

A general feature of the ^{23}Na NMR results is the coexistence of two separate lineshape components with substantially different spin-lattice relaxation times (T_1) and linewidths. As in previous studies of similar complexes, the long- T_1 and broad component is attributed to bound Na species while the short- T_1 and narrow component arises from mobile Na^+ ions.⁴ The ratio of the narrow line to broad line intensities as a function of reciprocal temperature is plotted in Fig. 3. That the difference between the lowest temperature value and the maximum value (occurring just above room temperature) is only about a factor of ten is indicative of the relatively minor role that "carrier generation" plays in the overall conductivity, which changes by more than four orders of magnitude over the same temperature range.

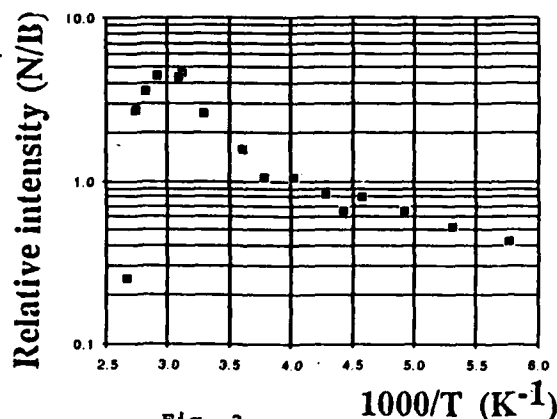


Fig. 3

The salting-out effect is manifested as a sharp drop in mobile ion concentration above $\sim 80^\circ\text{C}$. In addition, the slight decrease in N/B just after reaching its maximum value, which has been observed in other complexes⁴, is suggestive of an ion-pairing mechanism which, in fact, may be a precursor to salting-out.

Another example of the salting-out effect is evident upon viewing the data for PPO_8KSCN , shown in Figs. 4 and 5. For this material, the salt comes out of the polymer at a lower temperature, about 60°C as seen by a sharp endotherm at about 60°C in Fig. 4. That the material was complexed is shown by the single glass transition temperature at about -25°C . Once again, upon thermal treatment, the glass transition disappears with the appearance of an uncomplexed PPO glass transition. This material is interesting because the melting endotherms for the salt are at relatively low temperature as shown in Fig. 3a. As shown in Figs. 4b and 4c, similar endotherms are observed in the polymer after heating above 60°C . Since the salting-out effect occurs at a relatively low temperature, the effect on the electrical conductivity is quite dramatic as shown in Fig. 5.

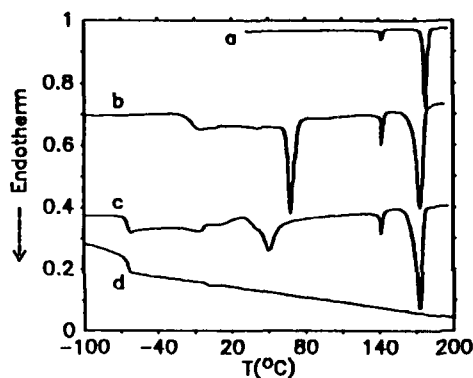


Fig. 4

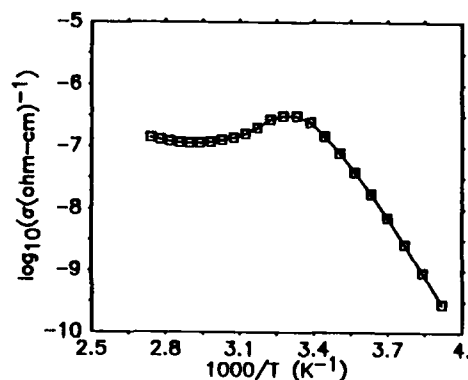


Fig. 5

ACKNOWLEDGMENTS

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SOLID STATE SODIUM CELLS WITH POLYMER ELECTROLYTE

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All-solid-state batteries with Li and an insertion material as active electrode components and *poly*-(ethylene oxide) based electrolyte has proven to be feasible alternatives to the classic secondary battery systems [1-2]. We have demonstrated, that also Na can be used as active material in this type of batteries [3]. The main incentive for replacing Li with Na is the generally higher conductivity of Na electrolytes, and the fact that Na does not form alloys with aluminium, making it possible to use this light metal - instead of nickel - for current collectors in bipolar cells. Furthermore Na is more abundant and less expensive than Li. These advantages will however be offset by a decrease in energy density caused by the higher molar mass of Na and the generally lower capacity of sodium insertion materials. In the present paper the behaviour of *poly*-(ethylene oxide)-sodium perchlorate electrolyte in all-solid-state cells will be discussed. $\alpha\text{-V}_2\text{O}_5$ is used as active component in the positive electrodes, as good cycling lives can be obtained with these electrodes. The operating temperature for these cells was chosen to 80°C, well below the melting point of Na (98°C).

EXPERIMENTAL

Electrolyte films were prepared by casting acetonitrile solutions of PEO ($M_w=4 \cdot 10^6$, BDH) and recrystallized NaClO_4 (Merck) on inert supports. After solvent evaporation the films were dried in vacuum (<0.01 torr) at 120°C overnight. This drying procedure of the casted films has proven to be of greater importance to the cycling behaviour than the dryness of the starting materials. The thickness of electrolyte films prepared this way was $\sim 50 \mu\text{m}$.

RESULTS AND DISCUSSION

The ionic conductivity of PEO-NaClO_4 films was measured at different salt concentrations as function of temperature. The results shown in fig 1 are consistent with results obtained for PEO-LiClO_4 [4]. Based on these results, the composition Na:O = 1:12 was chosen for further experiments. With this electrolyte composition an ionic conductivity of $6.5 \cdot 10^{-4} (\Omega \cdot \text{cm})^{-1}$ was achieved at the operating temperature (80°C).

Results of AC impedance measurements on symmetrical cells, with Na electrodes on both sides of the polymer film, are shown on fig 2.

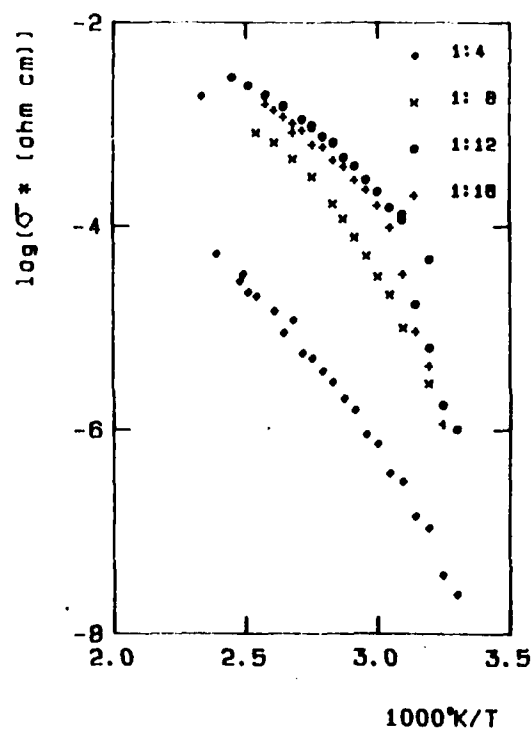


Fig 1: Ionic conductivity of PEO- NaClO_4 versus $1000/T$. The conductivities are calculated from impedance measurements with blocking electrodes.

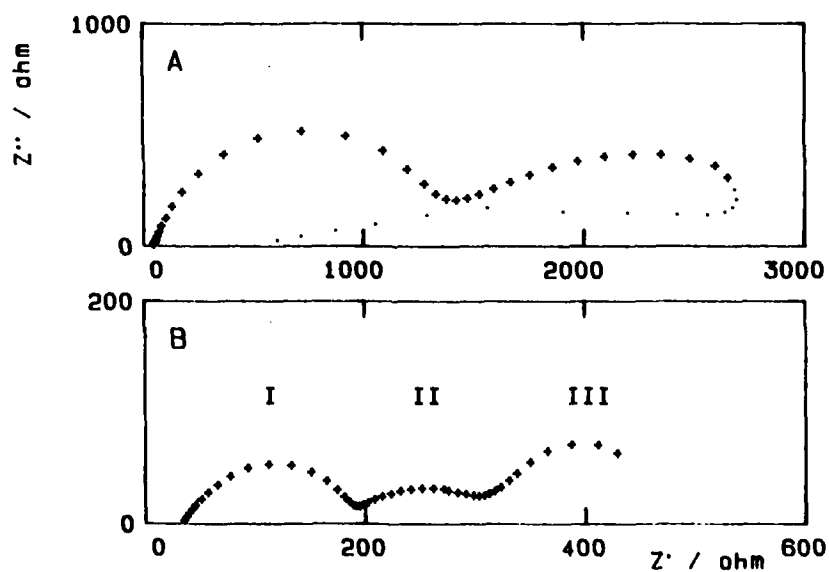


Fig 2: Impedance of $\text{Na} \mid \text{PEO NaClO}_4 (\text{Na:O}=1:12) \mid \text{Na}$ (80°C) cell. Electrode area = 0.7 cm^2 , electrolyte thickness $100 \mu\text{m}$. A: Immediately after assembly, B: After equilibration.

Fig 2.A shows the impedance of this cell shortly after assembly and heating to 80°C. The bulk resistance determined as the high frequency intercept with the real axis (45 Ω) is somewhat larger than expected from geometrical parameters (22 Ω), but the cell impedance is totally dominated by the large interfacial impedance. Two different relaxation arcs can be identified. The impedance of the cell is however not independent of time, as can be seen from the sudden decrease in low frequency impedance. The cell impedance stabilizes after a few hours, and the impedance measured the day after cell assembly is shown on fig 2.B. The interfacial impedance has now decreased considerably, and three distinct arcs are seen in the impedance plot. Tentatively the arcs can be ascribed to different phenomena, I: Resistance of an ionically conducting film on the sodium surface (220 $\Omega \cdot \text{cm}^2$), II: Transport in an inhomogeneous, porous layer (see [5]), and III: A diffusion arc caused by simultaneous transport of anions and cations in the bulk electrolyte [6]. From extrapolations of the width of arc III, and of the high frequency intercept, the transport number of Na^+ in the electrolyte is estimated to 0.2.

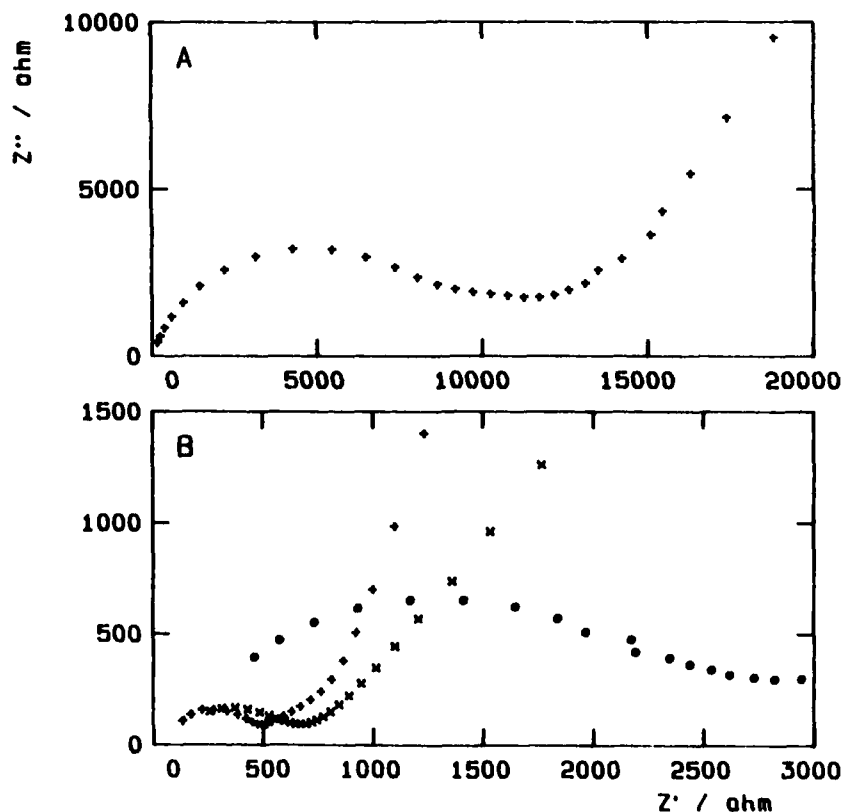


Fig 3: Impedance of $\text{Na} \mid \text{PEO-NaClO}_4 (\text{Na:O } 1:12) \mid \alpha\text{-V}_2\text{O}_5 (80^\circ\text{C})$ cell. Electrode area = 0.2 cm^2 , electrolyte thickness 100 μm . A: Immediately after assembly, B: + prior to cycling, x after cycle 15, o after cycle 69.

The symmetrical cells was found to be very prone to dendritic shorting, and failed in all cases after a few days. In order to monitor the long term stability of the Na-polymer interphase, AC impedance measurements were performed on complete cells with a Na negative electrode and a positive electrode consisting of 64 w/o α -V₂O₅, 9 w/o acetylene black, 19 w/o PEO and 8 w/o NaClO₄. These cells were much more stable towards dendrites, and could be cycled for months without shorting. In some cases dendrites formed (especially during the first few recharges), but they caused only temporary drops in cell voltage and vanished without causing any discernible decrease in cell performance. This phenomenon, often called "self healing" or "soft dendrites", is also known from Li conducting polymer electrolytes.

The impedance of the cell just after assembly, fig 3.A, show the same high frequency arc as seen in the symmetrical cell. Calculated on basis of Na electrode area an initial surface resistance of $1.8 \text{ k}\Omega\cdot\text{cm}^2$ is measured in both cell types. The low frequency pattern is however different, as this part of the impedance spectrum is dominated by the porous positive electrode.

A small current is drawn from the cell during the initial equilibration period, and the day after the assembly, the interfacial impedance has dropped to $\sim 90 \Omega\cdot\text{cm}^2$, fig 3.B. The cell is now cycled with a current density of $0.1 \text{ mA}/\text{cm}^2$ to a depth corresponding to uptake of 1.5 Na per V₂O₅. The interfacial impedance increases upon cycling; after cycle 15 it is $130 \Omega\cdot\text{cm}^2$, and after cycle 69, where the cell capacity has dropped to half of its initial value, a broad arc corresponding to $\sim 500 \Omega\cdot\text{cm}^2$ is obtained. At this point all Na in the cell has been cycled ~ 2 times.

When no current is drawn from a cell, a similar pattern is observed: initially the interfacial impedance decreases drastically, but upon prolonged stand it increases slowly again.

CONCLUSION

When properly prepared, PEO-NaClO₄ film can be used as electrolytes in all-solid-state Na cells. The high impedance of the Na/electrolyte interface seen just after assembly drops off to a value where it only gives a small contribution to the overvoltage during cell operation. Upon prolonged cycling an increase in the interfacial impedance is seen, possibly due to the formation of a porous layer on the Na/electrolyte interface.

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